Understanding and Quantifying Contaminant Discharges to Haytons Stream

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by

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“Water is the one substance from which the earth can conceal nothing; it sucks out its innermost secrets and brings them to our very lips”- Jean Giraudoux, 1946

Abstract

Haytons Stream, a headwater tributary of the Heathcote River/ Ōpāwaho, is consistently ranked with the worst water quality of all annually-monitored Christchurch city waterways, and has been reported to be a significant source of contaminants to the downstream Heathcote River (Margetts and Marshall, 2016; Marshall and Burrell, 2017). Previous investigations have shown that the stream is elevated in a number of contaminants (particularly trace elements, ammoniacal-nitrogen and dissolved reactive phosphorous). Haytons Stream drains a dense industrial land use catchment in Christchurch's Hornby and Wigram suburbs, with poor instream water quality thought to be a result of this heavily urbanised land use (commonly known as the 'urban stream syndrome'). However, previous studies have reported evidence of point-source discharges to the stream, suggesting that there are illicit discharges of contaminants from industry in the catchment. The sources of contaminants throughout Haytons Stream are still unclear, and the mechanisms for how and where contaminants are transported/discharged to the stream unknown.

This study adopted a multifaceted approach to understanding contaminants throughout Haytons Stream. Stream bed sediment was characterised for pseudo-total and labile/ bioavailable trace elements across the catchment, accompanied with three baseflow and three stormflow events of the stream water column for trace element, nutrient, suspended solid and *E. coli* concentrations. Potential subsurface pollution was monitored via continuous data logging of water level and conductivity trend in the catchment, to determine the occurrence of any dry-weather fluctuation in water level indicative of a discharge. Stormwater sumps on selected industrial sites were sampled, to gain a snapshot of potential industrial pollution that may contaminate Haytons Stream.

The bed sediment contained elevated concentrations of both pseudo-total and labile trace elements throughout the length of the stream, with particularly high concentrations of Zn across the catchment. These findings suggest that the bed sediment may be leaching metals back into the water column, and may be a key factor resulting in the very poor to non-existent instream ecosystem in Haytons Stream. Remediation, in the form of dredging, may be necessary to improve long-term water and ecosystem quality in the stream.

Instream sampling revealed that total and dissolved trace element concentrations were elevated during dry and wet weather, with several metals commonly exceeding ANZECC 80% species protection guidelines during baseflow. Upper catchment sites (within industrial land) generally had higher metal concentrations than lower catchment sites (re-landscaped/ pastoral land use), suggesting that the industrial land use is a major source of metals to the stream at all times. The Wigram Retention Basin in the lower catchment did not remove or decrease metal concentrations appreciably during baseflow, with metal concentration exports out of the basin common, leading to Haytons Stream polluting the

main stem of the Heathcote River with elevated trace element concentrations. Ammoniacal-N and dissolved reactive phosphorous concentrations spiked at the mid catchment site of Washbournes Road during dry and wet weather, suggesting a specific source of nutrients near this site. Wet weather sampling at this site in particular resulted in nutrient concentrations far in excess of ANZECC trigger values.

Continuous logging of water level revealed the frequent inappropriate discharge of contaminants to the stormwater network at Waterloo Road and Washbournes Road, represented by fluctuations (rises) in stream water level in absence of rainfall. At Washbournes Road, discharges observed from stormwater pipes were soapy or opaque-coloured, and can be tracked back up specific pipes to potentially responsible businesses. Discharges at Waterloo Road where the stream originates were frequently associated with hydrocarbon slicks, suggesting automotive or similar-based industries may be commonly (yet not solely) responsible for part of these discharges. As the stream emerges from the stormwater network at Waterloo Road, discharges could not be tracked further upstream. Therefore the upper catchment should be intensively targeted for further industrial pollution prevention and education, to avoid further industrial discharges to Haytons Stream via the stormwater network.

Conductivity logging revealed frequent wet weather pollution of nutrients (and subsequently conductivity trend spikes) at the mid catchment site of Washbournes Road. Small to moderate-intensity rainfall events produced large spikes in conductivity at this site (as well as elevated instream nutrient concentrations) which were not seen at the upper or lower catchment sites. This was corroborated with previous studies where a specific source(s) of nutrients in the mid catchment was identified, which was responsible for generating poor quality stormwater that eventually contaminates Haytons Stream (Brown et al., 1996).

Future research for pollution prevention in Haytons Stream or the wider Heathcote River would benefit from tracking of these mid catchment nutrients up the stormwater network to a specific source, and further understanding of the bioavailability of metals in sediment. Further research is also needed to understand the processes of absorption and release of contaminants from stream bed sediments in Haytons Stream or similar waterways. Greater implementation and uptake of at-source stormwater treatment (particularly for trace elements) would greatly benefit the water and sediment quality in the catchment, and is likely needed to mitigate the continual trace element pollution from the industrial land use. Expansion out of this catchment to conduct similar research on the neighbouring Curletts Stream (which has similar contaminant concentrations with a similar impact on the Heathcote River) would benefit the wider Heathcote River environment, whilst a continued strong pollution prevention and educational presence is recommended for both catchments.

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Abbreviations

ADD	Antecedent Dry Days
Al	Aluminium
A-N/NH_4-N	Ammoniacal-Nitrogen
APHA	American Public Health Association
As	Arsenic
ANZECC	Australian and New Zealand Environment Conservation Council
AVS-SEM	Acid Volatile Sulphide- Simultaneously Extracted Metals
BOD	Biochemical Oxygen Demand
Ca	Calcium
CCC	Christchurch City Council
Cd	Cadmium
Co	Cobalt
COD	Chemical Oxygen Demand
Cr	Chromium
CRM	Certified Reference Material
Cu	Copper
ºC	Degrees Celsius
DO	Dissolved Oxygen
DRP	Dissolved Reactive Phosphorous
ECAN	Environment Canterbury
E. coli	*Escherichia coli*
FC	Faecal coliforms
Fe	Iron
GC-FID	Gas Chromatography Flame Ionization Detector
GC-MS	Gas Chromatography Mass Spectrometry
HDPE	High-Density Polyethylene
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ISQG	Interim Sediment Quality Guideline
LMW	Low Molecular Weight
µg/L	micrograms per litre

µS/cm	micro Siemens per centimetre
mg/kg	milligrams per kilogram
mg/L	milligrams per litre
Mn	Manganese
Mo	Molybdenum
MPN	Most Probable Number
ml	millilitre
Ni	Nickel
NIWA	National Institute for Water and Atmospheric Research
NNN	Nitrate-Nitrite Nitrogen
PAH	Polycyclic Aromatic Hydrocarbon
%	Percentage
PP	Polypropylene
PVC	Polyvinylchloride
∑	Sigma (sum off)
SRM	Standard Reference Material
TC	Total Coliforms
Ti	Titanium
TKN	Total Kjeldahl Nitrogen
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorous
TPH	Total Petroleum Hydrocarbons
UC	University of Canterbury
US EPA	United States Environmental Protection Agency
V	Vanadium
VOC	Volatile Organic Compounds
WRB	Wigram Retention Basin
Zn	Zinc

Chapter 1 Introduction

1.1 Urbanisation of waterways

With the world's population increasingly concentrated in urban areas (estimated 60% of the human population by 2030), urbanisation is a widespread and rapidly-growing form of land-use change (Paul and Meyer, 2001). Urbanisation of land has been well-researched globally, with the land use change having marked effects on a watershed/ catchment (Hatt et al., 2004; Leopold, 1968; Walsh et al., 2005). Society is moving through an 'urban evolution' of water usage, transitioning from 'industrial-age built cities' amidst the industrial revolution to 'sanitary cities and suburbanisation' in the present day (i.e. cities with separate storm-sewer networks and greater human health protection). Future concepts of 'sustainable cities' with sustainable urban water modifications and enhancements are now forecasted for the future (Kaushal et al., 2015). These include transitions from large impervious surface coverage and use of channelised storm drains into controlled flow paths and improved stormwater management. With this, drainage and stream burial are anticipated to be replaced with new environmental regulation, land use planning and increased watershed protection (Kuashal et al., 2015).

With this said, the shift to modern-day suburbanisation has seen mass-urbanisation and increased impervious surface coverage over natural land, which can and has led to adverse effects on waterbodies draining such modified environments. Additionally, river catchments that drain industrial land (land uses with high percentages of impervious coverage and urban modifications/ activities) often suffer the worst effects of urbanisation, as they flow through highly modified and unnatural anthropogenic environments (Kim et al., 1998; Pekey, 2006; Sekabira et al., 2010).

The urban-derived effects on a watershed include increases in the speed and volume of surface runoff (a 'flashier' stream hydrograph), increased input of contaminants from urban municipal and industrial sources, and an overall reduced biotic richness/ diversity (Paul and Meyer, 2001; Walsh et al., 2005). These collective effects, and the additional characteristics of an urban stream environment (such as decreased channel complexities, reduced dry weather 'baseflows', increased contaminant loads and flashier hydrographs), are symptoms of the term 'urban stream syndrome' (Meyer et al., 2005; Walsh et al., 2005). The dominant drivers of these urban water impairments were recognised decades ago; being the increased coverage of impervious surfaces and the increased connectivity between terrestrial and aquatic environments. This is often via constructed stormwater drains and stream channelization (Brabec et al., 2002; Kaushal et al., 2015; Leopold, 1968; Wolman and Shick, 1967).

1.2 Impervious surfaces

An impervious surface can be defined as any material that prevents the infiltration of water into soil, with roads and rooftops most prevalent and identifiable, yet also encompassing pavements, patios, rock outcrops and/ or compacted soils (Arnold and Gibbons, 1996). With personal vehicles increasingly chosen over railway transport in the early 20th century, massive construction of highway systems and suburban growth have resulted in impervious surface coverage becoming synonymous with human presence and urbanisation (Arnold and Gibbons, 1996). Stream degradation has been reported to occur with levels of imperviousness as low as 10% (Center for Watershed Protection Inc, 1994), and as the natural landscape is further paved over, a change of events is initiated that typically ends in the degradation of water resources.

This change begins with alterations to the hydrological cycle of a catchment; in the way water is transported and stored. Urbanisation and increased impervious surface coverage alters a catchment's hydrological cycle; in that as imperviousness increases, there is a substantial reduction in deep water infiltration, with an accompanying large increase in surface water runoff (Figure 1.1). This is primarily through less area available for soil infiltration, and construction of impervious surfaces usually resulting in removal of permeable topsoil from a catchment, and replacement with impermeable concrete or similar material. Conventional stormwater drainage further reduces infiltration, ensuring that water draining off impervious surfaces during rainfall is transported directly to the nearest waterway, often through an underground reticulated pipe network (Walsh et al., 2004). These drainage systems were adopted with the principal concern of safety from stormwater runoff; to direct and drain water off paved surfaces as quickly and efficiently as possible (Arnold and Gibbons, 1996).

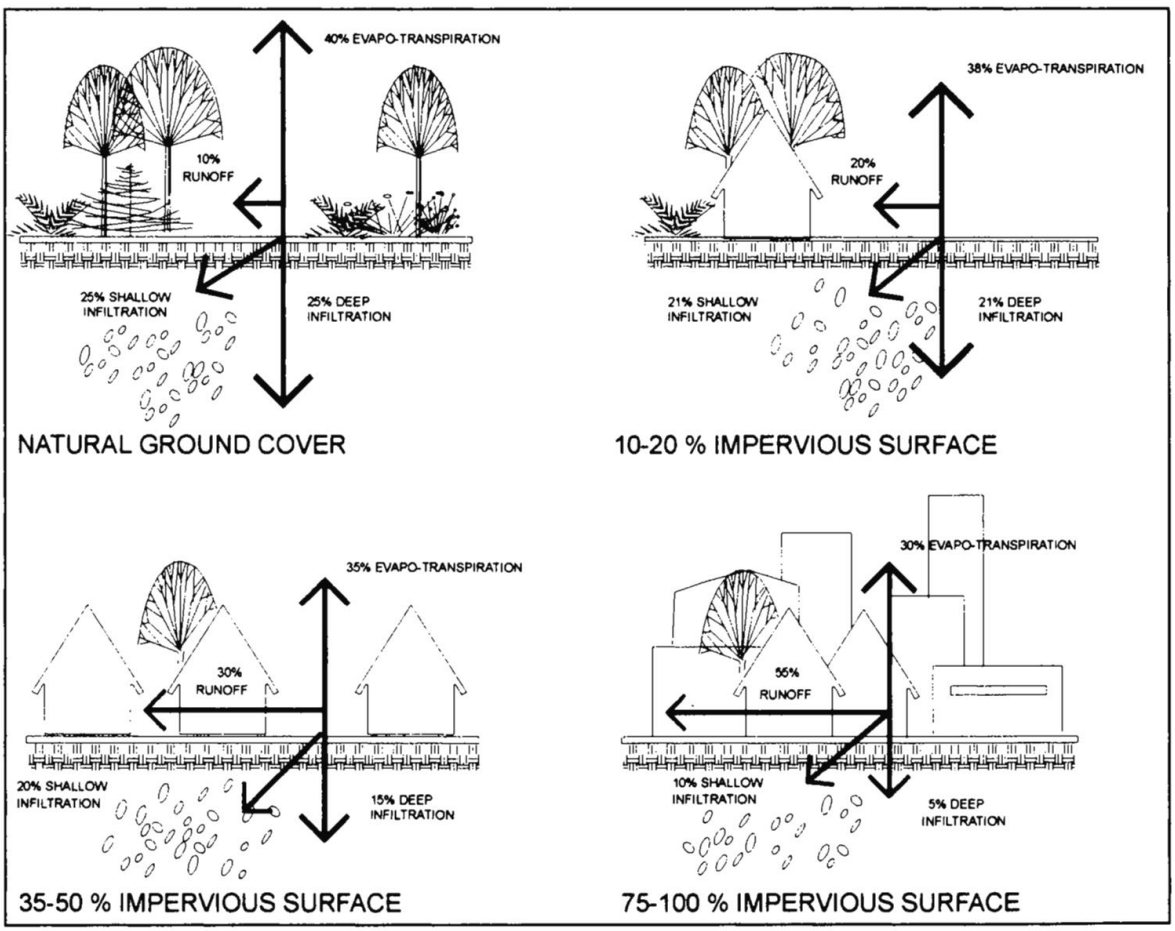

Figure 1.1 Hydrological changes associated with urbanisation (Arnold and Gibbons, 1996)

As impervious coverage increases in a catchment, a change in flow is one of the key physical changes from the modified hydrological cycle. In a stream with conventional stormwater drainage, baseflow levels are reduced, and every time the catchment receives sufficient rainfall, the stream will receive an almost immediate input of 'stormwater' through the constructed drainage pipes draining impervious land (Walsh et al., 2004). The lag time between rainfall falling on a piece of land and ending in a waterway is significantly altered with increased urbanisation (Figures 1.2 and 1.3). As water is transported faster across streets and roofs than naturally vegetated areas, there is a decreased lag time and increased peak rate of runoff (flood peak) (Leopold, 1968), resulting in more variable (or 'flashier') stream flows and hydrographs (Walsh et al., 2004). Another effect is the increased frequency of small to moderate increases in flow during smaller rain events (through direct surface runoff over impervious surfaces), and peak flows from larger rain events becoming larger, with high flows not as long-lasting (Walsh et al., 2004; Walsh et al., 2005).

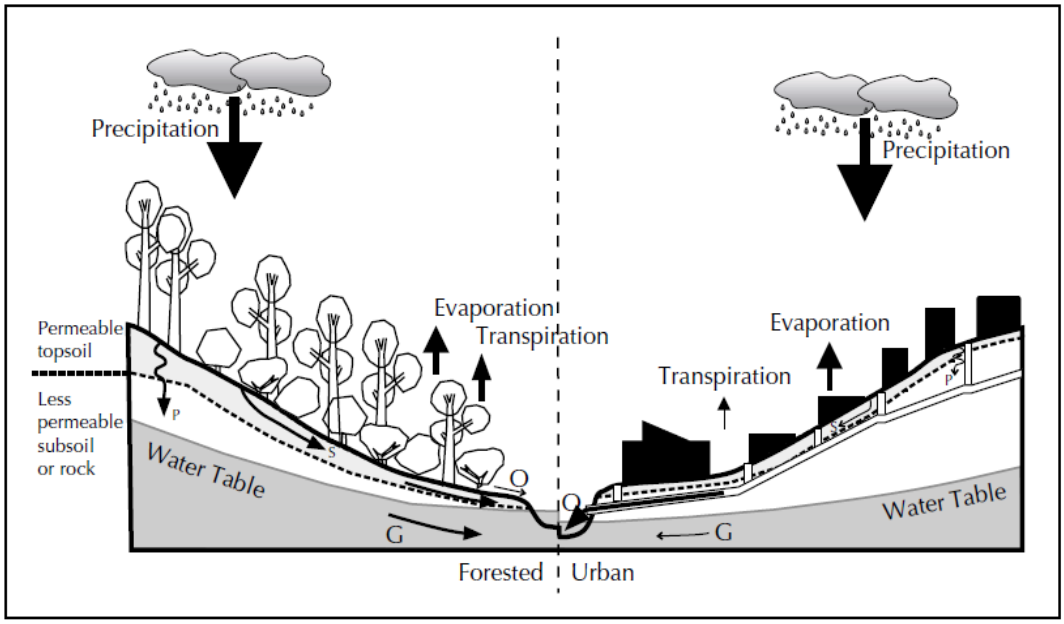

Figure 1.2 Differences between forested and urbanised catchments, seen through increased overland flow (O), decreased subsurface flow through soils (S), reduced percolation (P) and subsequent reduced groundwater recharge (G) (Walsh et al., 2004)

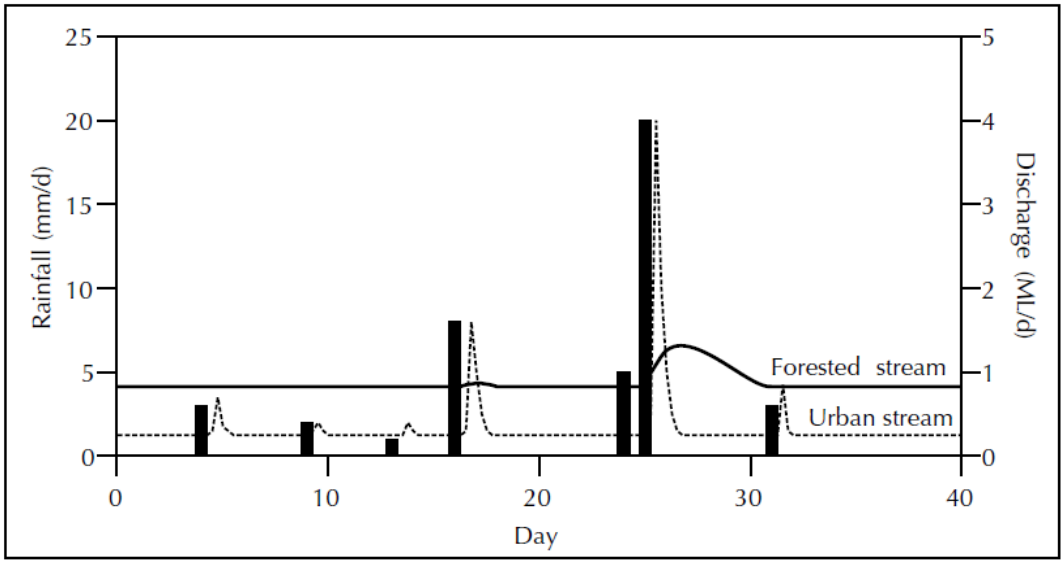

Figure 1.3 Schematic hydrograph comparison between a forested stream and an urban stream, with hypothetical catchment sizes of 1km^2 (Walsh et al., 2004)

A decrease in subsurface infiltration can reduce groundwater recharge and water tables. This can threaten water supplies and reduce the groundwater contribution to streamflow, potentially resulting in intermittent drying-up of streams during periods of low flow (i.e. summer) (Arnold and Gibbons, 1996; Leopold, 1968).

These physical modifications and the increased connectivity between terrestrial and aquatic environments through stormwater infrastructure often result in additional inputs of urban-derived sediment and contaminants into waterways (Walsh et al., 2004; Walsh et al., 2005). The increased sedimentation, flash flooding potential and characteristic low riparian vegetation cover seen in urbanised catchments can result in changes to the geomorphology within urban catchments. Although urban streams may be modified by human activity for convenience and safety, for example for flood management, natural channel dimensions of urban streams are altered over time by long-term modifications in sediment supply and bankfull discharge (Leopold, 1968). These long-term modifications of natural processes result in urban waterways tending to have increased frequency of erosive flows, increased channel width, pool depth and an overall decrease in channel complexity compared to forested streams (Violin et al., 2011; Walsh et al., 2005).

1.3 Water chemistry in urban catchments

The chemical impacts of urbanisation on a waterway are more variable than the hydrologic/ geomorphic effects, and are dependent on; the extent and type of urbanisation (i.e. residential versus industrial), presence of waste water treatment plant effluent/ sewer overflows, and the extent of the stormwater drainage system (Niemczynowicz, 1999; Paul and Meyer, 2001). In the absence of anthropogenic impacts, natural concentrations of nutrients, suspended particulate matter, salts and other substances in-stream will vary catchment to catchment, determined by the local bedrock and soil composition, rainfall, and characteristics of catchment vegetation (Walsh et al., 2004). In undeveloped catchments, potential 'contaminants' are usually efficiently removed by terrestrial processes, resulting in water quality that is typically high. With urban land-use, there are several contaminants that are not present in undeveloped catchments, which can be highly detrimental to water quality and aquatic ecosystem health (Walsh et al., 2004). Urban stream water chemistry is usually typified by increased water temperature, nutrient content, trace elements/ metals, organic contaminants and microbes (Paul and Meyer, 2001; Walsh, 2000; Walsh et al., 2004; Walsh et al., 2005). The extent of urbanisation is thought to be main control on instream water chemistry, implying that the greater level of urbanisation imposed upon a watershed, the higher the concentrations of these contaminants will be present (Paul and Meyer, 2001).

1.3.1 Urban stormwater runoff and sources of urban contaminants

Non-point source pollution, being the diffuse wash-off of contaminants deposited on constructed surfaces, has been identified as one of the major causes of deteriorating quality of receiving waters (Lee and Bang, 2000). As urban infrastructure is often designed to collect precipitation and transport it out of the watershed, usually via existing surface channel waterways, the quality of that surface water runoff, seepage water and groundwater is influenced by the pollutants that collect on impervious surfaces (Göbel et al., 2007). There are four major categories of stormwater contaminants; particulates

(sediment), trace elements/ metals, Polycyclic Aromatic Hydrocarbons (PAHs), and nutrients (Table 1.1). Depending on catchment characteristics microorganisms can also become important contaminants to consider. These pollutants are all sourced from a wide variety of urban land-uses and activities (Aryal et al., 2010).

Table 1.1 Sources of pollutants in stormwater runoff (Aryal et al., 2010)

	Soil erosion	Vehicles	Human/animal waste	Fertilisers	Household chemicals	Industrial processes	Paints and preservatives
Solids							
Metals							
Oil,grease and organics							
Nutrients							

1.3.1.1 Particulates

TSS (Total Suspended Solids) is a measure of the total mass of suspended particulates in water, typically originating from exhaust gas, traffic, asphalt, building erosion and sand/ silts transported by wind (Aryal et al., 2010). Impacts of TSS can include increased turbidity, decreased light penetration and decreased resultant activity and growth of photosynthetic organisms in an aquatic environment. Sediment itself can also clog fish gills, smother aquatic habitats and gradually accumulate toxic pollutants with the settling of suspended particles (Aryal et al., 2010).

The size distribution of suspended sediments has a significant influence on stream water quality. Sansalone and Buchberger (1998) studied particles in runoff from an urban freeway, with their results showing that urban runoff from paved surfaces transports a wide gradation of solids ranging in size from 1µm to greater than 10,000µm. Studies of runoff from motorways in France have shown that runoff samples contained around three quarters of fine particles (<50µm) (Andral, 1999), with most observed cases having particles in runoff less than 75µm in size (Aryal et al., 2010).
In other studies, over 50% of metals were found sorbed to particles less than 43µm (Sartor and Boyd, 1972). In their study, although fine solids only contributed just 5.9% of the total solids collected, this sediment contained one-third to one-half of all algal nutrients, three-quarters of total pesticides and over half of all metals. Finer sediments have a greater affinity to bind higher trace element concentrations than coarse sediments (Aryal et al., 2010; Duncan, 1995; Taylor and Owens, 2009; Zanders, 2005). For example, Horowitz and Elrick (1987) and Zanders (2005) reported strong correlations between elevated trace element concentrations, and high proportions of samples with particles sizes falling in between <63-<125µm.

1.3.1.2 Trace elements

Sources and pollutant build-up

Trace element presence is perhaps the most distinguishable aspect of urban stream water chemistry. Many trace elements are the product of urbanisation of a catchment; sourced from industrial, commercial and residential areas, which can accumulate on impervious surfaces and flush off to receiving waters with sufficient rainfall (Aryal et al., 2010; Göbel et al., 2007; Horowitz and Elrick, 1987; Pitt et al., 1994). Trace elements are of particular importance in runoff because of their toxicity, omnipresence and persistence in the environment over long timescales (Aryal et al., 2010; Davis et al., 2001). A list of the most common trace elements and stormwater pollutants with their likely sources are presented in Table 1.2, with shaded areas indicating pollutant sources.

The three stormwater metals most commonly studied are copper, lead and zinc, reported in 'particulate' and 'dissolved' forms (Brown and Peake, 2006; Göbel et al., 2007). Higher concentrations of these metals are typically found in greater intensities of urban and industrial land uses, due to the higher presence and density of their potential sources in these environments (Aryal et al., 2010; Brown and Peake, 2006; Davis et al., 2001; Göbel et al., 2007; Huber et al., 2016).

Table 1.2 Possible sources of pollutants in road runoff (Aryal et al., 2010)

	Brakes	Tyres	Frame and Body	Fuel and Oil	Pavement	Litter
Cadmium						
Chromium						
Copper						
Iron						
Iron						
Lead						
Nickel						
Zinc						
Organic Solids						
Inorganic Solids						
PAHs						

Davis et al. (2001) estimated metal loadings from separate urban sources, showing that approximately 75µg of Cu, 3µg of Pb and 89µg of Zn per vehicle-km were released from vehicle brakes alone. Vehicle brake emissions (for copper) and tire wear (for zinc) are important metal sources, whilst atmospheric deposition is a source of cadmium, copper and lead (Davis et al., 2001). This vehicle tyre and break wear dust accumulates on impervious surfaces (e.g. busy urban roads) and washes off to nearby waterways during rainfall events (Davis et al., 2001; Zanders, 2005). Copper and zinc in stormwater are commonly sourced from roofing materials as well, with the majority in roof runoff released in the

free-ion, bioavailable phase (Karlén et al., 2002; Karlén et al., 2001; Pennington and Webster- Brown, 2008). Studies local to New Zealand have shown that during storm events, runoff can generate metal concentrations in the thousands of µg/L (Charters et al., 2017; Charters et al., 2016; O'Sullivan et al., 2012; Pennington and Webster- Brown, 2008). Wicke et al. (2014) concluded that older galvanised roofs were a more substantial source of metals in rainfall runoff than newer roofs, and that as rainfall pH decreased, dissolved portions of Zn and Cu exponentially increased.

Pollutant (including trace element) load build-up on impervious surfaces increases with antecedent dry periods, but is not a limiting factor when determining total wash-off loads; with wash-off itself most strongly associated with rainfall intensity (Duncan, 1995). Duncan's (1995) summary stated that transport of pollutants in urban runoff is predominantly through suspended solids, natural organic and artificial human litter. Key pollutants are strongly associated with suspended solids, with roadsides and busy urban areas generating high concentrations of sediment runoff a key source of trace elements to the environment (Brown and Peake, 2006; Zanders, 2005; Zhang et al., 2014).

Toxicity to aquatic organisms

Once 'in the environment', trace elements are found in both the water column and in sediment (Rainbow, 2002), where they can accumulate in tissues, organs and bodies of organisms at concentrations dependant on the organism and element of concern (Eisler, 1983). Aquatic organisms react differently to different phases of metals; as a macrophytic alga will react to dissolved metal sources only, in contrast to a suspension feeder that will be affected by both dissolved and particulate phases, and a deposit feeder that will react to metals available in sediment (Rainbow, 1995). Many trace metals are toxic to a wide variety of aquatic organisms, having the potential to significantly affect organism community functions and structure, whilst some trace metals accumulate in organisms and up food-webs (Bryan and Langston, 1992; Clements, 1991; Klerks and Weis, 1987; Prosi, 1981).

In contrast to non-essential elements (such as lead, cadmium or arsenic), the essential elements such as copper, zinc, iron and cobalt have important biochemical functions in aquatic and terrestrial organisms. However, if concentrations at the source of supply (e.g. food/ water) are too high, homeostatic mechanisms which can regulate metal content in the organism fail to function, and these essential trace elements can act in a chronic or acutely toxic manner (Prosi, 1981). Bioaccumulation of trace elements has been shown to occur in a wide range of aquatic organisms, including mosses, lichens, invertebrates, and fish and bird species (Basile et al., 2008; Gundacker, 2000; Labrecque et al., 1995; Pourang, 1995). Trace element ingestion, uptake and accumulation can be through the water column (dissolved or particulate elements), sediments, ingestion of fine-grained particulates, organics, or through feeding and

food-chain processes via other aquatic organisms (Bryan, 1971; Gundacker, 2000; Medeiros et al., 1983; Pourang, 1995; Widianarko et al., 2000).

1.3.1.3 Sediments as heavy metal reservoirs

Sediments are often viewed as indicators of metal contamination within an urban environment, due to the ability of sediments to accumulate and bind metals over time (Duzzin et al., 1988; Lee et al., 2000). Most metals partition onto particulate matter such as clay minerals, Fe/Mn oxides/ hydroxides, carbonates, organic substances and biological materials (Calmano et al., 1993; Yu et al., 2001). Importantly, natural and anthropogenic activities have the capacity to remobilise contaminated sediments and release contaminants from sediment and sediment pore water back into the water column. These remobilisation events can range from daily tidal currents in coastal settings, to high wind energies and storm events, where turbulent flow conditions can expose anoxic sediments to oxic conditions, resulting in potential contaminant remobilisation (Calmano et al., 1993; Eggleton and Thomas, 2004). Additional geomorphic features can influence sediment metal concentrations. Higher concentrations have been found in areas of low velocity, where fine sediments and organics can accumulate (Paul and Meyer, 2001), showing further reasoning why urban streams with lower flow and finer sediment commonly contain elevated metal concentrations. The route of entry of metals to aquatic organisms appears to be through both direct exposures to dissolved metals, and ingestion of metals associated with fine sediments and organic matter (Paul and Meyer, 2001). This has led to further research stating that metal toxicity is greatest in the riverbed, not water column, and that runoff into streams could reduce toxicity during input, but increase toxicity in the long-term (House et al., 1993; Medeiros et al., 1983).

1.3.1.4 Hydrocarbons

Hydrocarbons are organic compounds arranged in varying structural configurations, composed primarily of carbon and hydrogen atoms. Hydrocarbons are classified into two main divisions; aliphatic and aromatics, which can then be broken down into smaller subdivisions (World Health Organisation, 2005). Petroleum products are created through crude oil fractionation, which produces different products for the many different uses of petroleum. There are significant compositional differences between petroleum products due to their different uses and sources; therefore these compositional differences (e.g. between gasoline, diesel, aviation fuel and heating oil) result in hydrocarbon ‘fractions’, which classify compounds according to their composition and behaviour in soil and/ or water (United States Environmental Protection Agency, 2017; World Health Organisation, 2005). The main processes dictating environmental concentrations of petroleum products are volatilisation, biodegradation and dissolution in water. Only a small portion of hydrocarbons are significantly soluble in water (i.e. resulting in oil slicks floating on water surfaces), with water solubility dictating the nature

of contaminant present. The term Total Petroleum Hydrocarbon (TPH) refers to the analytical method to determine presence, where compounds are put into fractions, and analysed/ reported in that manner (results are commonly reported back in varying C-bands, which relate to grouped hydrocarbon compounds, compositions and weights) (World Health Organisation, 2005).

Due to their wide variety of uses, TPHs can enter the environment in many ways. This can commonly be from accidental spills, industrials releases or through commercial/ private by-products. The main cause of elevated TPH concentrations is commonly through accidental spillage or a short-term incident (World Health Organisation, 2005).

Exposure to high concentrations of TPHs can lead to damaging human and animal effects (especially juveniles). Some TPH compounds (e.g. benzene, toluene and xylene) can affect human central nervous-systems, causing headaches and dizziness. Others have been shown to harm the lungs, skin, blood and immune system. Animal effects have similarly been seen on the lungs, central nervous system, liver and kidneys, whilst other compounds have been shown to affect the reproductive system (Agency for Toxic Substances and Disease Registry, 1999).

Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons comprise a large class of organic compounds of fused benzene rings, including both natural aromatic hydrocarbons and synthetic hydrocarbons for industrial usage (Yamamoto et al., 1997). Therefore, anthropogenic PAHs (excluding high-temperature incomplete combustion processes such as vehicle usage) are likely the result of industrial effluent discharges or episodic spill events (Paul and Meyer, 2001). Aside from point-source discharges (spills or intentional illicit discharges), urban land surfaces (i.e. stormwater runoff) and urban air have also been identified as a primary source of PAHs to urban waterways (Lopes and Bender, 1998). Natural sources of PAHs can be from volcanic events or forest fires; however the dominant source remains from anthropogenic activities that can wash off as stormwater runoff or through industrial discharge (Landrum et al., 1987). In freshwater, PAHs are heavily associated with suspended organic and particulate matter, where they are expected to transfer rapidly from the water column to instream sediments.

Water PAH concentrations can be significantly higher near industrial area outlets (Wild and Jones, 1995). PAHs can be toxic (including acutely) to aquatic organisms depending on the structure of the molecule, resulting in potential alteration of DNA leading to mutagenesis and carcinogenesis (Landrum et al., 1987; Meador et al., 1995; Varanasi, 1989). PAHs can change (increase) in toxicity through UV radiation and light-activation, via photosensitization reactions and potentially by photomodification of the chemical structure (Huang et al., 1993; Landrum et al., 1987). The major health concern from PAHs is when they undergo metabolic transformation into mutagenic, carcinogenic and teratogenic agents,

where these can bind to and disrupt DNA and RNA. PAHs are therefore listed as priority pollutants by the United States Environmental Protection Agency (USEPA) (Wild and Jones, 1995).

1.3.1.5 Nutrients

Nutrients (nitrogen and phosphorous) are essential elements in all aquatic environments, that have negative impacts when found in excessive levels (Aryal et al., 2010; Mueller et al., 1996). Common sources of nutrients to waterbodies include chemical fertilisers applied to agricultural land, lawns and gardens, whereas residential and industrial areas have been found as major sources of nutrients due to urban stormwater runoff (Chessman et al., 1992; Wernick et al., 1998). Typically analysed species of phosphorous include total phosphorous, soluble reactive phosphorus and biologically available phosphorous, of which, phosphate is a key form present in stormwater runoff, primarily measured as soluble or dissolved reactive phosphorous (Aryal et al., 2010). Nitrogen is found in organic and inorganic forms, and is measured as total nitrogen, Kjeldahl nitrogen, nitrate and nitrite nitrogen, and ammonia-nitrogen (Aryal et al., 2010). Many of these forms are found in synthetic substances and are indicative of anthropogenic pollution (Aryal et al., 2010; Walsh et al., 2005). Urban centres have been shown to increase the nitrogen concentration in rivers for hundreds of kilometres (Meybeck, 1998), with the extent of increase depending on depending on wastewater treatment technology, degree of illicit discharge, leaky sewer lines, and fertiliser use (Paul and Meyer, 2001).

Elevated nutrient concentrations in streams can lead to eutrophication or intense nutrient enrichment in aquatic environments. Excess nutrients can result in increased biomass of algae, phytoplankton and periphyton, reduced water clarity, odour and taste, shifts in fish compositions to more undesirable species (including increased probability of fish kills) and decreased aesthetic value of a waterbody (Carpenter et al., 1998; Smith et al., 1999).

1.3.1.6 Pathogens

Urbanised catchments typically display higher bacterial densities, with excessive faecal coliforms most frequently related to the density of housing, population, percent impervious area and domestic animal density (Mallin et al., 2009; Paul and Meyer, 2001; Young and Thackston, 1999). Sources can be diffuse during rainfall wash-off as well as from point-sources, with high values in dry weather not uncommon, potentially indicating leaky sewer systems or illicit discharges (Paul and Meyer, 2001). Combined sewer overflows, nearby wastewater treatment plants or animal faeces can also be sources of pathogens to urban waterways (Mallin et al., 2009; Young and Thackston, 1999). Common pathogens in urban streams include viruses, bacteria and protozoa, which can be a direct threat to human health upon contact or ingestion (Arnone and Walling, 2007). However, a common indicator for faecal pollution

and for public health protection is *Escherichia coli* (*E. coli*) (Edberg et al., 2000). *E. coli* is present in all mammal faeces, but does not multiply appreciably in the environment, as well as being relatively inexpensive and simple to test for. Thus, *E. coli* is used world-wide as a proxy for microbial freshwater contamination (Edberg et al., 2000).

1.3.2 Point-source discharges

The USEPA's Nationwide Urban Runoff Programme highlighted the significance of pollutants from illicit entries into urban stormwater drainage systems. These entries (essentially flow from storm drain outfalls during dry weather) could be the result of direct illicit connections or indirect unintentional connections, such as leaky sanitary sewage contributions through infiltration (Pitt, 1993). Pollutant contributions during dry-weather flows have been shown to be high enough to significantly degrade receiving water quality, due to their large contribution to the annual mass pollutant loading (Field, 1994; Pitt, 1993). A study of dry and wet-weather discharges in Toulouse, France (a city with similar stormwater infrastructure to New Zealand; with separate storm and sewer systems) found that dry weather discharges had a significant impact on annual catchment pollution loads, and that the extent of urbanisation at the outlet was an important factor for higher pollutant loads (Deffontis et al., 2013).

Pitt (1993) noted that, due to dry weather entries potentially contributing to pollution during both summer and winter months (in addition to stormwater runoff), much less pollution reduction benefit will occur if focus is placed solely on stormwater drainage. Dry weather discharge sources can be split into three main categories of residential, commercial or industrial sources. Residential and commercial sources include sanitary wastewater sources, automobile maintenance and operation, irrigation, or groundwater/ potable water infiltration from leaking water mains. From this, sanitary wastewater is the most significant source of bacteria, whilst automobile maintenance and operations are significant sources of toxicants. Industrial sources commonly include cooling or rinse water, other process wastewater and/ or sanitary wastewater. Sources tend to be related to the raw materials used, final product, and the waste/ by-products created in the industrial process (Field, 1994; Pitt, 1993).

There is higher potential for unauthorised connections within older industries, one reason being that during the time of that industries development, sanitary sewers were yet to exist (Pitt, 1993). Additionally, when industries expand or change, there is a possibility for illicit connections through floor or storm drains which should be, but are not, treated prior to disposal. Industries processing large volumes of water may find that sanitary sewer capacities are inadequate or are too far away, resulting in improper removal of excess water via the stormwater drainage system. Continuous processes such as industrial manufacturing are important because their waste streams are likely to be constantly flowing, allowing easier detection of a dry-weather discharge. Most of these continuous discharges will likely

be undiluted and have discernible characteristics such as increased odour and/ or colour (Field, 1994; Pitt, 1993).

When assessing the contamination of an urbanised stream, it is important to consider the wide variety of pollution sources available. Non-point source pollution from stormwater runoff is clearly an important factor in urban stream pollution, however the importance of point-source discharges to a stream should not be ignored when assessments of the sources and effects of contaminants on urban streams are to be studied. Dry-weather discharges are often the most polluting and environmentally degrading, contributing large proportions of annual contaminant loads in one or few events. For this reason, urban stream restoration and water quality improvements must begin with cessation of point-source discharges to a waterway, before tangible improvements can be seen.

Locally, in New Zealand, the inception of the Resource Management Act (1991) enabled local government authorities to reduce the impacts of point-source pollution on the environment, placing enforceable laws and penalties onto environmental 'noncompliance' (New Zealand Government, 1991). The Canterbury Regional Council (Environment Canterbury) has a statutory responsibility under the Resource Management Act 1991 to work towards the sustainable management of the regions natural and physical resources (Environment Canterbury, 2017). Christchurch City Council, the local government responsible for Christchurch City itself, has duties under the Local Government Act and requirements from separate stormwater management consents/ plans to routinely monitor surface water and sediment quality across Christchurch City (Margetts and Marshall, 2016).

1.3.3 Stormwater sumps

Drainage systems and stormwater sumps have potential to hold substantial quantities of abrasion products and pollutants (such as particulates and metals), with road surfaces being a significant source. The most common stormwater drainage system is a 'sump', which drains the road surface into a box that extends 0.5-1 metre below the bottom of the outlet. This structure is also known as a catch basin or gully pot (Pitt and Field, 1998). The conventional sump is designed to attenuate flow through underground piped drainage systems, and act as a settling tank for road runoff-sourced solids before their mixing and discharge to the network (Morrison et al., 1988). The modest sizes of sumps means that the retention time of runoff during most storm flows is under five minutes (Butler et al., 1995). Although sump liquor quantities are typically small (< 100 litres), for a whole catchment the volume is significant (Butler et al., 1995), as up to 20% of the mean volume discharged by studied runoff's have been found to come from stored sump volumes (Mance, 1982). Sumps have been used extensively over the past 100 years, mainly to reduce sedimentation issues in stormwater drainage systems (Pitt and Field, 1998). The ability for sumps to trap sediment is varied, with the median particle size captured ranging between 300-3000 µm, with less than 10% comprising of particles <100 µm (the typical upper

limit of particles in runoff). This results in sumps being able to trap and store the largest runoff particles, yet allowing the finer (and more proportionally contaminated sediments) to flow straight through the structure (Butler et al., 1995; Pitt and Field, 1998).

A 2-year study in Bellevue, Washington, USA reported that at any one time, twice as much polluted sediment was found in stormwater drainage systems than on the street surface. As the chemical quality of sediment in the sumps were similar to street sediment, most of those sediments were likely washed off from the street during rainfall but were not directly discharged out of the system (Pitt, 1985). Brown and Peake (2006) analysed sediment from stormwater sumps in Dunedin, New Zealand for heavy metals and PAHs. The concentrations of Cu, Pb and Zn exceeded the ANZECC Interim Sediment Quality Guidelines (ISQG) low (and ISQG-high for zinc), and were similar to previously reported road-derived materials in North America (Stone and Marsalek, 1996), where street sediments were found to contain heavy metal concentrations that would adversely impact receiving water quality.

Supernatant sump water quality predominately has two separate states; during dry and wet weather. During dry weather, the dissolved oxygen concentration rapidly decreases, resulting in anaerobic conditions, and the release of oxygen-demanding soluble organics, sulphides and ammonium, as well as changes in the distribution of metal species between dissolved and insoluble phases (Butler et al., 1995; Morrison et al., 1988). During wet weather, incoming stormwater displaces the standing 'sump liquor' which can represent a significant contribution to pollutant load outflow. The quality of sump water discharged to the stormwater system and downstream receiving environment is therefore affected by the two main processes. These are, 1) erosion of pre-existent sediments in the sump (via incoming flow scouring the deposited sediment and re-suspending contaminants for export) and, 2) the discharge of interstitial sediment water and overlying water that is of poorer quality than incoming stormwater (Pennington and Kennedy, 2008).

Three different stormwater control devices were tested by Pitt & Field (1998); comprising a conventional inlet with a sump and two devices with filters (one fine filter fabric and one with courser mesh). After comparing inflow and outflow stormwater, they found that only the catch basin sump resulted in significant pollutant removals. These were for suspended solids (30% average), turbidity (40% average), colour (15% average) and total solids (20% average). No other pollutants (including metals, organic and inorganic contaminants) were found to be significantly reduced, in any of the stormwater devices (Pitt and Field, 1998).

Morrison et al. (1988) studied gully pots (sumps) in the UK before and after storm events, finding that whilst during low-intensity storms, gully pots could act as small-scale detention basins for solids, these deposits were readily removable by high-intensity storms, which often resulted in significantly increased metal loadings compared to the inflows. The same study also found that whilst the overall soluble metal content of inflow to outflow water was similar, the soluble metals leaving gully pots were

predominantly in a bioavailable form, which will further contribute to the ecologically-damaging effect of exiting stormwater. Morrison et al. (1988) also stated that flushing/ cleaning of gully pots should ideally occur at 4-7 day intervals to provide maximum control on metal outflows, and that any less-regular maintenance cannot be expected to make valuable contributions to the removal of toxic pollutants from runoff.

In contrast, Memon and Butler (2002) concluded with their model that frequent cleaning of sumps does not result in an appreciable impact in runoff quality. Their study modelled only very slight reductions in suspended solids, chemical oxygen demand and ammonium with weekly cleaning, finding that increasing the pot volume tended to result in increased solid retention and capture of ammonium. International and local examples illustrate that there can be a wide variation in the contaminant concentrations and impacts of sediment and 'sump liquor' in sumps to receiving waters at the end of drainage systems, and that these outgoing concentrations are very dependent on the land-use activities that surround the sump. Although the above research is congruent that stormwater sumps can harbour ecologically-detrimental concentrations of contaminants, the effectiveness of regular cleaning, optimal design and maintenance of sumps seems to be an ongoing question (Memon and Butler, 2002). This will likely have to be resolved at a local level through localised sump sampling and analysis, to determine contaminant concentrations in sump water and therefore their localised polluting-potential.

1.4 Ōpāwaho/ Heathcote River Catchment

The Heathcote River/ Ōpāwaho extends for approximately 26 kilometres from south-west Christchurch, New Zealand to its mouth at the Avon-Heathcote Estuary/ Ihutai. Spring-fed headwaters create the baseflow, where the river flows around the edges of the basalt and agglomerate Port Hills, across the Tertiary/ Quaternary-aged gravels that thin to the gravel, clay, sand, silt and peat deposits of eastern Christchurch towards the coast. The river was likely established in its location due to occasional flood spillages from the Waimakariri River along the base of the hills, creating a flood passage that was maintained by hill runoff (Canterbury Regional Council, 1998; Christchurch City Council, 2016).

The catchment (Figure 1.4) covers approximately 103 km^2 in south Christchurch and drains a variety of land uses that are predominantly residential, as well as significant industrial areas in Sockburn, Hornby and Woolston (Christchurch City Council, 2016). The Heathcote/ Ōpāwaho contains approximately 86 km of waterways on the Port Hills and 105 km on the flat, with a drainage network comprising 1,500 km of stormwater pipeline mains greater than 600 mm in diameter, most of which convey untreated stormwater runoff to nearby surface waterways (Christchurch City Council, 2016). The Ōpāwaho/ Heathcote River's surface water network contains dry plain tributaries in the west and Port Hills, and Cashmere Stream, a flowing tributary. It is thought that the plain tributaries (Paparua Stream, Haytons Stream, Awatea Stream and Curletts Stream) were fed by spring flow until the early European times, evidenced by the fact that Maori used the upper Ōpāwaho/ Heathcote River as a waka route as far as Owaka Rd in Hornby (Christchurch City Council, 2016).

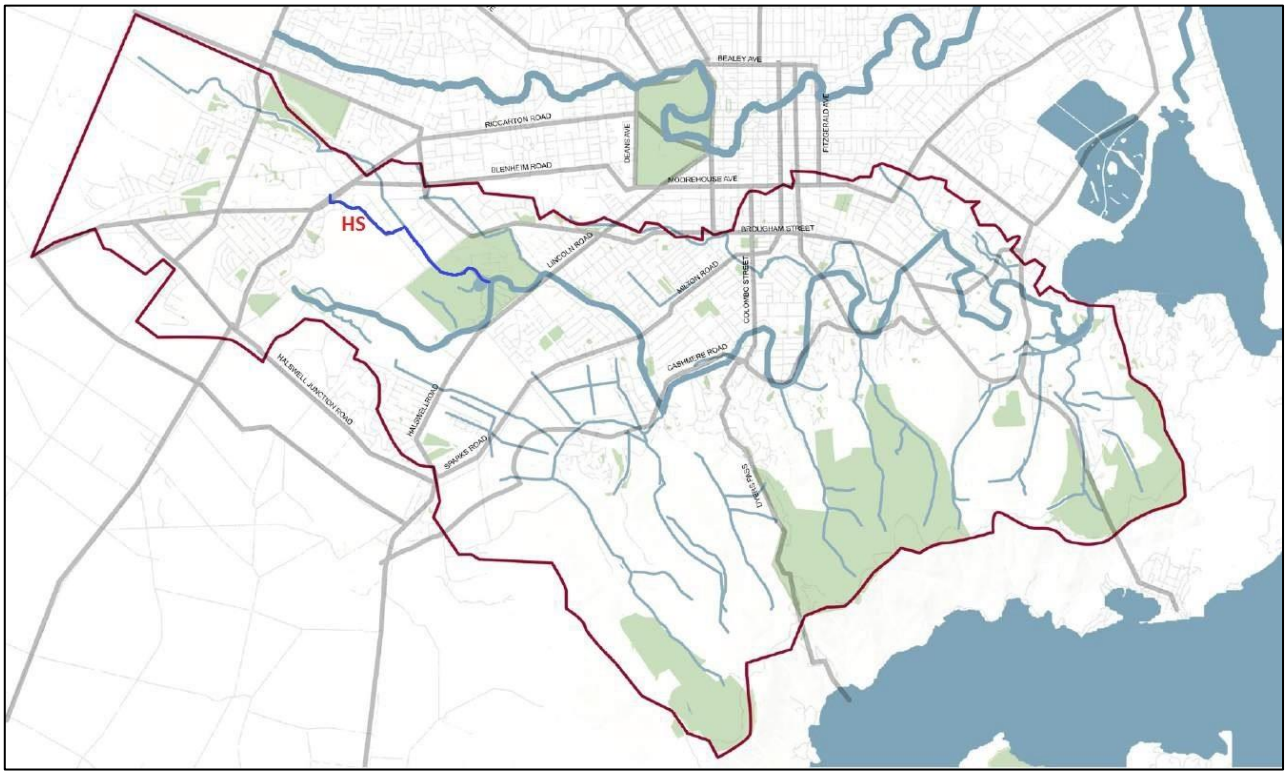

Figure 1.4 Ōpāwaho/Heathcote River catchment in the context of wider Christchurch (HS- Haytons Stream) adapted from (Christchurch City Council, 2016)

The landscape of the lower Ōpāwaho/ Heathcote River was converted to pasture and orchard land in the 1850s, with industrial development occurring rapidly in the lower catchment between 1880 and 1925 (Deely, 1991; Wilson, 1989). Before 1971, over 10 million litres of industrial effluent per day were directly discharged into the river from over 150 firms. Between 1971 and 1973, after the construction of the Woolston industrial sewer, all effluents were pumped to the Christchurch Drainage Board treatment plant, allowing water and sediment quality to considerably improve (Deely, 1991).

However, ongoing development and extensive settlement within the catchment over the last two centuries, combined with the 2010/11 Canterbury Earthquake Sequence have meant that catchment values are still degraded (Christchurch City Council, 2016).

1.5 Water and sediment quality within Christchurch City

In 2006/07, Pattle Delamore Partners (PDP) were commissioned by Environment Canterbury to conduct an analysis of water quality data from 1992-2006 for the Avon/ Ōtākaro and Heathcote/ Ōpāwaho Rivers, with their results showing that both rivers are lowland streams with heavily urbanised catchments that exhibit water quality problems typical of urban land-use impacts. This included nutrient enrichment and microbial contamination in both rivers, whilst the Heathcote had issues with ammoniacal-nitrogen and suspended solid concentrations (Pattle Delamore Partners, 2007).

Sediment quality has been assessed in Christchurch streams on several occasions, with the Heathcote River catchment having metal concentrations increasing from rural to residential, with mixed-urban and industrial-urban showing the highest concentrations (Kingett Mitchell Ltd, 2005). This study and other subsequent studies (Gadd, 2015; Gadd and Skyes, 2014) have shown that waterways across Christchurch contain elevated concentrations in bed sediments, with some metals regularly exceeding ANZECC guidelines, particularly for Zn and Cu. One area of concern that is consistently outlined in water and sediment quality surveys is Haytons Stream (previously Haytons Drain). Sediment surveys from 1988 show that Haytons Stream was a concern for cadmium, copper, lead and zinc, with the first three exceeding the ANZECC Interim Sediment Quality Guideline (ISQG) low, and the later (zinc) exceeding the ISQG high (Kingett Mitchell Ltd, 2005). ANZECC sediment quality guidelines for selected metals are listed below in Table 1.3.

Table 1.3 Recommended sediment quality guidelines for metals (ANZECC, 2000)

Metal (mg/kg dry weight)	ISQG-Low (Trigger Value)	ISQG-High
Antimony	2	25
Cadmium	1.5	10
Chromium	80	370
Copper	65	270
Lead	50	220
Mercury	0.15	1
Nickel	21	52
Silver	1	3.7
Zinc	200	410

Annual surface water quality monitoring is conducted by Christchurch City Council (CCC) as a requirement for stormwater management consents and the creation of stormwater management plans. These annual reports have identified the tributary of Haytons Stream to be of especially poor water quality, consistently ranking it as the worst (or one of the worst) site in the Heathcote River catchment based off catchment scale and number of placings as 'worst site' for measured parameters across Christchurch (Margetts and Marshall, 2016; Marshall and Burrell, 2017).

1.5.1 Haytons Stream catchment

Haytons Stream is a headwater tributary of the Heathcote River/ Ōpāwaho in Christchurch, New Zealand, draining a mixed land-use catchment of industrial and residential land-use in south-west Christchurch. The catchment covers an area of approximately 13km^2, encompassing two main sub-catchments; Paparua Stream and Haytons Stream (Moores et al., 2009). Haytons Stream drains the southern part of the catchment (Figure 1.5), which is located centrally in the catchment as a whole, emerging from a reticulated stormwater network that drains an area of heavy industrial land-use, including logistical freight transport, construction, automotive industry and some residential activity (O'Sullivan and Charters, 2013). The stream emerges from the network as open-channel flow for approximately 600 metres, before re-entering the network for a similar distance. The stream re-emerges in an area of industrial land use before its confluence with Paparua Stream. Below this confluence (around Lodestar Avenue), Haytons Stream runs through areas of industrial and re-landscaped pastoral/ agricultural land before entering the Wigram Retention Basin (WRB), the outlet of which discharges almost directly into the Heathcote River (Moores et al., 2009). The Christchurch West Melton water zone (created as part of the Canterbury Water Management Strategy) have identified Haytons Stream as a priority catchment within Christchurch, due to its historically high levels of pollution.

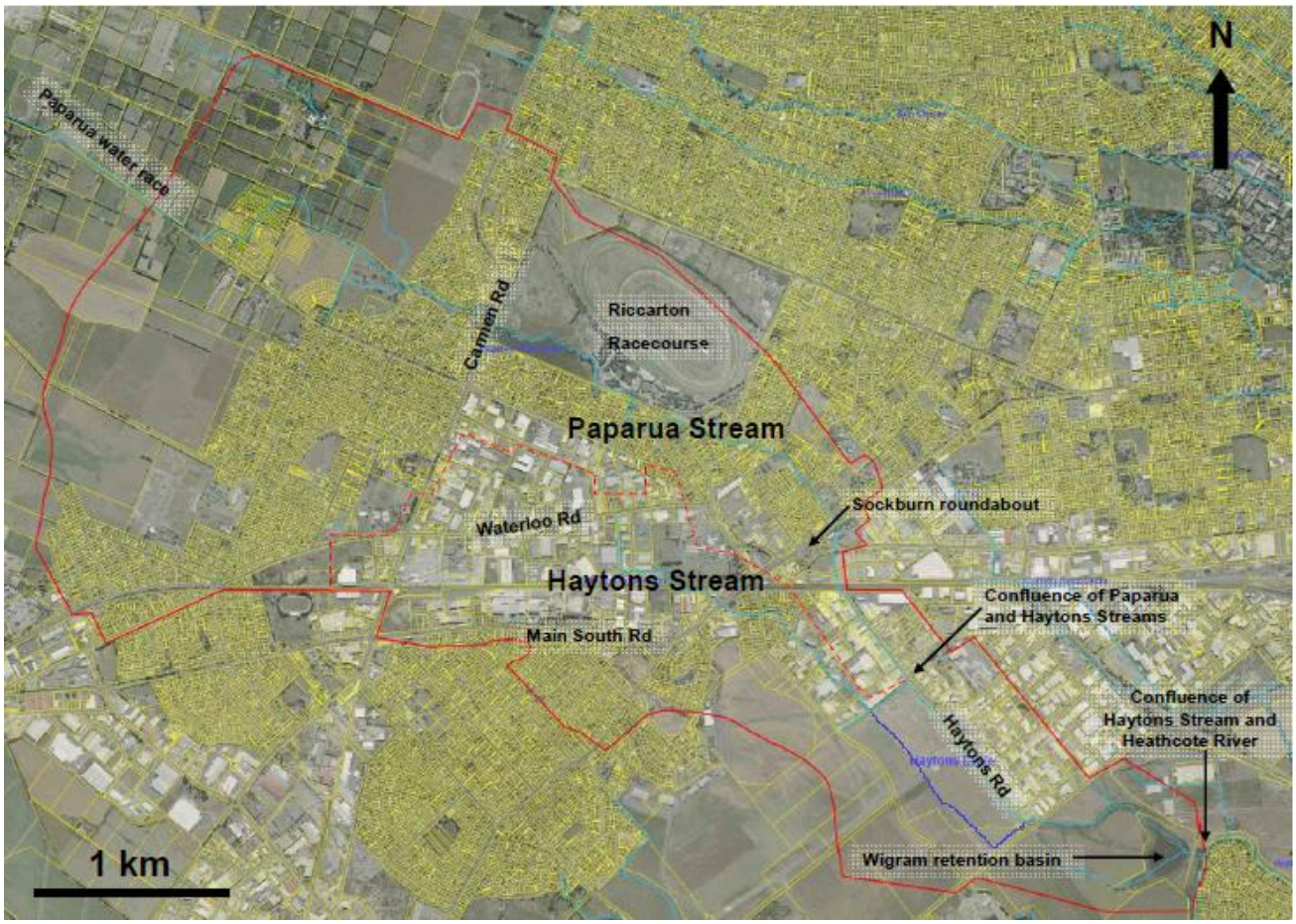

Figure 1.5 Haytons Stream catchment showing catchment boundary (solid red line), sub-catchment boundary between Haytons and Paparua Streams (dashed red line), land-use (dense yellow lines represent residential areas, large white/grey roofs are industrial). Solid dark blue line represents the new stream alignment. Edited from (Moores et al., 2009)

1.5.2 Haytons Stream water and sediment quality

1.5.2.1 Water quality

Christchurch City Council's annual monitoring reports of city-wide surface water quality consistently outline Haytons Stream as one of the worst if not worst site for water quality in Christchurch (Margetts and Marshall, 2016). The synthesis of 15 years of water quality data from Pattle Delamore Partners (2007) indicated that Haytons Stream is a source of suspended solids, BOD, nutrients (ammoniacal-nitrogen and dissolved reactive phosphorous) and microbiological contaminants to the Heathcote River. Of the samples taken from Haytons Stream, 40-50% were above the 0.9 mg/L toxicity guideline for ammonia-nitrogen, and DRP concentrations were up to 10 times the guideline value for risk of adverse ecosystem effects. Downstream of the confluence with Haytons Stream, the Heathcote River has elevated concentrations of these nutrients, which gradually decrease yet remain well above guideline values. Instream trace element concentrations were also elevated, with copper, lead and zinc consistently exceeding the ANZECC guideline for a 95% level of freshwater species protection (guidelines presented in Table 1.4). (Pattle Delamore Partners, 2007).

Table 1.4 ANZECC trigger values for different stormwater metals at different levels of protection (ANZECC, 2000)

Common stormwater metals	Trigger values for freshwater (µg/L)			
	Level of protection (% species)			
	99%	95%	90%	80%
Cadmium	0.06	0.2	0.4	0.8
Chromium (Cr_{VI})	0.01	1.0	6	40
Copper	1.0	1.4	1.8	2.5
Lead	1.0	3.4	5.6	9.4
Nickel	8	11	13	17
Zinc	2.4	8.0	15	31

After Haytons Stream exists industrial land, the land use turns pastoral, where it flows into the Wigram Retention Basin (WRB), and flow is retained/ stored before underground pumping. The stream then resurfaces before direct confluence with the Heathcote River. Crude estimates have stated the retention time of water in the basin to vary between 198 days (low inflow) to 36 days (high inflow) assuming an estimated pond capacity of 340,000 m^3 (Christoffel, 1995). The WRB has been found to be efficient in the removal of suspended solids, yet its performance varied for other forms of contaminants, where net exports of nitrate and dissolved metals to the Heathcote River during storm events have been found (Brown et al., 1996). Recent research has shown that the basin has an important role in improving water quality before the Heathcote River confluence. Decreases in turbidity and various nitrogen species, pH neutralisation, as well as the conversion of inorganic nitrogen to higher organic nitrogen content have

been seen downstream of the basin (Silveira et al., 2016). However, the effectiveness of trace element removal has not been assessed.

A 2009 investigation by the National Institute of Water and Atmospheric Research (NIWA) into the water and sediment quality of Haytons Stream found that Haytons Stream had a poorer water quality than Paparua Stream, and that water quality improved after Paparua appeared to 'dilute' Haytons Stream downstream of their confluence. Water quality was generally poorest at the sampling sites of Gerald Connolly Place (HAS-GCP) and Symes Road (HAS-SYR). Dissolved metal concentrations did not change substantially during wet weather, and elevated concentrations of ammoniacal-nitrogen, oxidised nitrogen (NO_x-N), DRP, BOD and zinc were measured during both dry and wet weather, indicating that discharges of these contaminants are not restricted to urban stormwater runoff (Moores et al., 2009). On numerous site visits, there were visible surface sheens and odours coming from the stream, indicating discharges during dry weather. Ammoniacal-N concentrations were highly elevated at times, reaching 14-100 mg/L, far beyond concentrations of 0.01-0.1 mg/L typical in natural waterways (Meredith and Hayward, 2002).

Dry weather sampling resulted in ammoniacal-N concentrations of 2.5-33 mg/L on average at HAS-GCP, and up to 33 mg/L in stormflow. DRP concentrations were highest at HAS-SYR and remained elevated throughout storm events, suggesting a constant discharge of DRP that kept concentrations at values rarely seen in natural waterbodies (Moores et al., 2009).

The 2009 NIWA investigation coupled two Manta 2 data sondes (one in Paparua and one in Haytons Stream) to continuously log water temperature, dissolved oxygen (DO), conductivity, pH and turbidity, as well as ammoniacal-nitrogen and stream water level. Comparison and analysis of the results with local rainfall data showed that whilst major peaks in the stream hydrograph corresponded with rain events, there were smaller fluctuations in the water level that were independent of weather conditions (Moores et al., 2009). Haytons Stream exhibited a diurnal variation in water level of up to 50mm, indicating regular (daily) discharges to the stream, followed by periods of two days when discharges must have ceased. Most interestingly, there were many separate events on different dates when stream water level, conductivity, turbidity and ammoniacal-N concentrations spiked in the stream in dry weather, independent of any rainfall that could result in urban stormwater runoff (Figure 1.6). Ammoniacal-N concentrations also spiked on the data sondes after rainfall, confirming that contamination of Haytons Stream with ammoniacal-N can occur during both dry and wet weather (Moores et al., 2009).

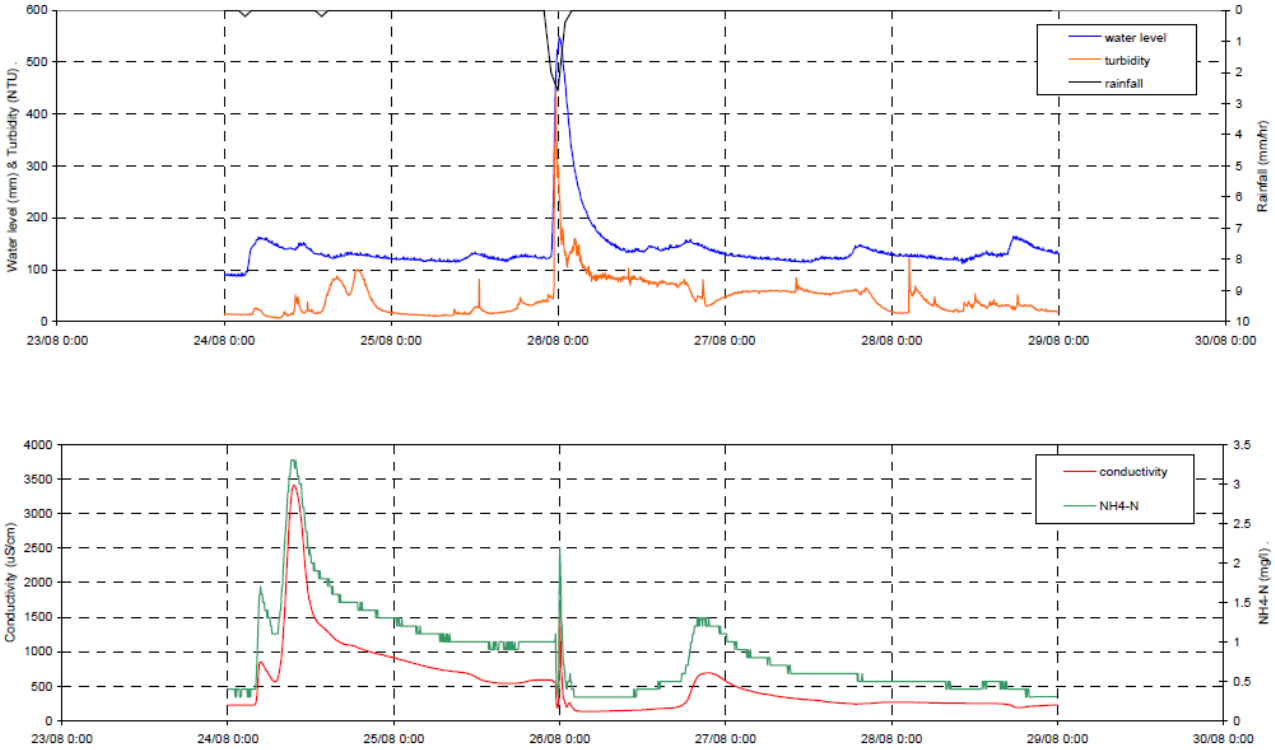

Figure 1.6 Example of data sonde results in Haytons Stream, showing spikes in conductivity and ammoniacal-N that are independent of a rainfall event (Moores et al., 2009)

A second water quality investigation was conducted in Haytons Stream in 2013 by the University of Canterbury, to determine if there were visible water quality improvements in the stream since the 2009 investigation (O'Sullivan and Charters, 2013). This investigation was specifically at Gerald Connolly Place, as this was one of the worst sites in 2009, and physical modifications of the lower stream restricted sampling at the time. The study conducted very similar investigations to Moores et al. (2009), using automatic samplers for water chemistry, water level and turbidity logging, as well as a suite of in-situ grab samples for analysis (O'Sullivan and Charters, 2013).

O'Sullivan and Charters' (2013) study corroborated the findings of the 2009 investigation, finding that Haytons Stream water level exhibited increases during baseflow conditions in dry weather. This, coupled with visible observation of pipe discharges, and visible sheens/ scums and odours from the stream, confirmed that Haytons Stream (at least at Gerald Connolly Place) was still receiving point-source discharges as well as non-point source stormwater runoff during wet weather (O'Sullivan and Charters, 2013). The study found that water quality in Haytons Stream was still in a degraded state and had not improved since 2009, characterised by elevated nutrients, metals, and suspended solids with a low DO and fluctuating pH. Pollutant concentrations were generally higher in 2013 than in 2009, for example total copper concentrations in the water column were up to 22 times the 80% ANZECC trigger value of 2.5µg/L in storm events, with total zinc concentrations consistently exceeding the 80% trigger

value of 31µg/L during baseflow, and both total and dissolved zinc reaching 33 times that value during stormflow (O'Sullivan and Charters, 2013). This study noted that whilst diffuse pollution may be one answer to heavy metal contamination, the concentrations of heavy metals in the Haytons Stream bed sediment may be a source of metals to the water column, particularly for Zn.

1.5.2.2 Sediment quality

A summary of relevant historical sediment metal concentration studies across the Heathcote River/ Ōpāwaho catchment is provided in Table 1.5 below. A recent review of Heathcote catchment sediment indicated that sediment quality is poorer in Curletts and Haytons Streams than in the Heathcote River, and that the contaminant of highest concern is zinc, which frequently exceeded the ANZECC ISQG-high guideline (Gadd, 2015). The most recent sediment surveys concerning Haytons Stream are from Kingett Mitchell Ltd (2005) and Moores et al. (2009). Kingett Mitchell's study found that Haytons Stream sediments were elevated in lead above the median value of 51 mg/kg, which is just above the ANZECC ISQG-low (sampling results of 66.1 and 101 mg/kg), while zinc concentrations were highest in Haytons and Curletts Streams, with the highest concentration just downstream of Haytons Stream (Kingett Mitchell Ltd, 2005). Concentrations of zinc greatly exceeded the ANZECC ISQG-high guideline of 410 mg/kg, indicating significant contamination of the bed sediments. Moores et al. (2009) conducted a more thorough sediment survey of the Haytons Stream bed, finding that there were no obvious differences throughout the catchment for sediment quality. Zinc was elevated at all sites, exceeding the ISQG-low at two sites (downstream of the Wigram Retention Basin and Hayton Road), whilst the other two sites (Gerald Connolly Place and upstream of the retention basin) had zinc concentrations exceeding the ISQG-high guideline, suggesting potential for adverse effects in biota living in or near these sediments (Moores et al., 2009).

As the previous sediment sampling in the Haytons Stream catchment was approaching 8 years ago, the current concentrations of trace elements in the bed sediments are unknown. Re-characterisation is needed to interpret if this ongoing degradation of Haytons Stream water quality is influencing and degrading sediment quality. Water quality is measured every year as part of CCC's monitoring requirements, yet is only sampled at the Wigram Retention Basin outlet in the lower catchment, meaning that the last intensive water quality investigation throughout Haytons Stream for trace elements was in 2013 at Gerald Connolly Place (O'Sullivan and Charters, 2013), and down the length of the stream in 2009 by Moores et al. (2009).

Table 1.5 Summary of previous Heathcote River sediment data (adapted from Gadd, 2015)

Location	Survey	# sites	Cadmium (mg/kg)	Chromium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)	Nickel (mg/kg)	Zinc (mg/kg)
Curletts and Haytons Drains	Robb (1988)	5	2.2 ±3.4	22 ±12	83 ± 99	154 ±229	7.3 ± 4.1	454 ±354
	KML (2005)	4	-	-	97 ± 81	152 ± 151	-	736 ±101
	NIWA (2009)	8	-	-	15 ± 8	32 ± 18	-	492 ± 585
Upper Heathcote	Robb (1988)	14	1.1 ± 1.4	12± 3	81 ± 93	70 ± 52	7.2 ± 1.9	173 ± 93
	KML (2005)	7	-	-	50 ± 40	45 ± 16	-	616 ± 295
	NIWA (2009)	2	-	-	34 ± 40	40 ± 31	-	385 ± 106
	Golder (2012)	1	1.3 ± 0.1	16 ± 1	73 ± 2	31 ± 2	9.6 ± 0.3	393 ± 15
Mid Heathcote	Robb (1988)	7	0.47 ± 0.29	9 ± 2	20 ± 8	80 ± 76	6.8 ± 1.3	156 ± 53
	KML (2005)	2	-	-	30 ± 12	47 ± 29	-	276 ± 16
	Golder (2012)	1	0.45	21	54	50	14	410
Lower Heathcote	Robb (1988)	28	0.41 ± 0.27	77 ± 101	43 ± 29	208 ± 247	12 ± 4	269 ± 130
	KML (2005)	5	-	-	35 ± 18	56 ± 26	-	380 ± 253
	Golder (2012)	2	0.2 ± 0.2	20 ± 12	16 ± 13	23 ± 18	11 ± 3	161 ± 127

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1.5.2.3 Ecological state of the Haytons Stream catchment

Aquatic assessments of Haytons Stream near and within the Wigram Retention Basin have shown that these areas have poor ecological health, with extremely low invertebrate species diversity and abundance (McMurtie, 2002; Ward and Meurk, 1995). These studies have outlined lower Haytons Stream to have a homogeneous in-stream habitat, smothered in anoxic mud near the Wigram Basin with an especially depauperate invertebrate community, dominated by pollution and heavy metal-tolerant chironomids and oligochaetes, which themselves are found in low numbers (McMurtie, 2002). The significant amount of sedimentation documented around the Wigram Retention Basin, particularly just upstream of the inlet, indicates long-term substrate changes from a stony substrate to one with >300 mm of fine sediment cover. This has created an unstable habitat and anoxic benthic environment that would prevent the presence of any of the EPT (Ephemeroptera, Plecoptera and Trichoptera) macroinvertebrates whose presence indicates a good water quality (McMurtie, 2002).

The Wigram Retention Basin is primarily in place to reduce flood risk, retain and treat contaminants from the upper catchment, and provide a level of protection for the downstream aquatic environment. McMurtie (2002) found that although the basin somewhat achieves these tasks, the invertebrate community was still very low and lacked any clean water EPT taxa. The basin has also been shown to fail to deal with a concentrated slug of fluoride pollution in the catchment that was found above and below the basin at high concentrations (Brown et al., 1996).

The aquatic ecosystem within Haytons Stream and the Wigram Retention Basin clearly reflects the poor water and sediment quality that is consistently found throughout the catchment. Any substantial shift in aquatic ecosystem composition and health will likely not be seen until water and sediment quality is considerably improved, as well as any existing intentional or accidental concentrated discharges of contaminants to the stream ceased.

1.6 Thesis aims and objectives

The aims of this thesis were to identify and quantify contaminant discharges to Haytons Stream, and better understand the sources, mechanisms and conditions for how contaminants are transported to the stream. These aims had an overarching goal of ceasing industrial point-source discharges and increasing understanding of contaminants for improved stormwater/ pollution management, to improve long-term water quality in Haytons Stream. Improving Haytons Stream water quality will lead to decreasing the impact this stream has on the downstream Heathcote River/ Ōpāwaho.

The research objectives were:

1. To characterise a wide range of trace element concentrations in the bed sediments along Haytons Stream (to assess the possibility of legacy contamination and release of metals from the sediment to the water column). Pseudo-total and labile/ bioavailable fractions were analysed as well as Total Organic Carbon and Total Phosphorous content.

2. To quantify total and dissolved trace element concentrations in the water column of Haytons Stream during baseflow and stormflow, ten sites in the catchment were sampled during three baseflow and three stormflow events. Three specific sites along the stream were also chosen to conduct additional contaminant analysis (for ammoniacal-nitrogen, TSS, DRP, NNN and *E. coli*) during these sampling runs, to further understand instream contaminants and their potential sources. Samples for hydrocarbons/ nutrients were occasionally taken at sites, depending on the character of the stream (presence of visible sheens/ odours) at the time of sampling.

3. To identify spatial and temporal industrial discharges of contaminants to Haytons Stream during dry weather, using continuous monitoring of water level and conductivity loggers throughout the catchment. Analysis of the loggers' results created direction for targeted grab sampling of discharges, which were then analysed for chemical signatures and indication of source(s).

4. To determine the potential contribution of individual industrial sites to the pollution/ contamination of Haytons Stream, a one-off grab sampling campaign from key industrial stormwater sumps was undertaken over the course of the study.

1.7 Thesis structure

The thesis is divided into five chapters describing the separate components and objectives of the research:

I. Chapter one introduced background and relevant literature to the project, including the effects of urbanisation on watersheds, urban stormwater runoff and the sources and effects of contaminants in urban streams.

II. Chapter two discusses the one-off characterisation of the bed sediment along Haytons Stream for trace element, total organic carbon and total phosphorous content.

III. Chapter three outlines and discusses the results of the baseflow, stormflow and reactive water sampling throughout Haytons Stream.

IV. Chapter four discusses the installation and results of the continuous data loggers and the sampling from stormwater sumps in the catchment.

V. Chapter five amalgamates the important findings and further implications of this study for future management/ research within the catchments of Haytons Stream and the Heathcote River/ Ōpāwaho.

Chapter 2 Characterisation of trace element concentrations in the bed sediments of Haytons Stream

2.1 Introduction

Urban areas can generate significant volumes of pollutants entering receiving waterways, from numerous potentially contaminating activities, industries and materials. Contaminants collected on impervious surfaces can be washed off with sufficient rainfall, and ultimately transported to receiving waterways through stormwater drainage infrastructure (Arnold and Gibbons, 1996; Paul and Meyer, 2001; Walsh, 2000). Urban stormwater runoff is a major source of trace element contamination in urban streams, with trace elements frequently studied due to their potentially high toxicity, omnipresence and environmental persistence (Aryal et al., 2010; Davis et al., 2001; Paul and Meyer, 2001). After stormwater runoff enters a receiving waterway, trace elements (metals) have an affinity to bind to fine-grained sediment particles in the water column and stream bed. Metals commonly partition onto the particulate matter of clay minerals, Fe/Mn oxides/ hydroxides, carbonates, organic and biological materials within sediment matrixes (Duzzin et al., 1988; Lee et al., 2000). This can often result in sediments holding higher metal concentrations in the riverbed than in the water column, leading to sediments acting as a useful indicator of metal contamination within an urban environment (Duzzin et al., 1988; House et al., 1993; Medeiros et al., 1983). Accumulated contaminants in sediment can ultimately affect instream biota, where concentrations can eventually have adverse impacts to any organism living in or near the contaminated sediment (ANZECC, 2000).

Sediment metal concentrations throughout Christchurch are monitored by Christchurch City Council on a 5-yearly catchment-rotational basis, whereby a different catchment is monitored for sediment every year. Although the Heathcote/ Ōpāwaho catchment was last surveyed in 2015 (Gadd, 2015), Haytons Stream was not included and was last sampled intensively in 2009 by Moores et al. (2009). A recent stream re-alignment means that parts of lower Haytons Stream have not been previously sampled for sediment metal concentrations.

In this recent survey of the Heathcote River (excluding Haytons Stream), city outfall drain, Linwood canal and the Estuary drain within Christchurch City, lead and zinc were the trace elements that regularly exceeded ANZECC sediment quality guidelines (Gadd, 2015). This study noted that Haytons and Curletts Streams have been previously identified as having poor sediment quality, and that stormwater management efforts should actively be made in those catchments. Studies in other smaller Christchurch streams that are not routinely monitored by councils have shown that sediment and water samples still regularly exceed ANZECC guidelines (Blakely and Harding, 2005; O'Sullivan et al.,

2012), showing that trace element contamination and reduced biotic diversity are environmental issues not solely restricted to the major waterways of Christchurch City.

In 2009, the results of Haytons Stream sediment surveys were restricted to the common stormwater metals of Cu, Zn and Pb (Moores et al., 2009). This study showed that, of the three metals, zinc was of highest concern, exceeding the ANZECC ISQG-low at half of the sites, and the ISQG-high at all other sites. This most recent study concluded that Haytons Stream sediments were not substantially more contaminated with copper or lead than other Christchurch streams, but that zinc was consistently a problem in Haytons Stream, having a median value higher than most Christchurch streams, with the maximum value the highest of all sites in Christchurch (Moores et al., 2009).

There is little reporting for a wider range of sediment trace element concentrations other than these three common stormwater metals within Christchurch, including within the Haytons Stream catchment. As previous sampling of Haytons Stream sediment was approaching eight years ago (as of 2017), there is a need for updated sampling throughout the catchment, to assess the extent of sediment contamination since the previous analysis. Additionally, contaminant concentrations (including total and dissolved metals in the water column) were higher in 2013 than in 2009 in Haytons Stream (O'Sullivan and Charters, 2013), suggesting that the contamination of the stream with trace elements has been ongoing.

This chapter describes the characterisation of Haytons Stream bed sediments, analysing for a wider range of trace elements than previously conducted, and analysing for the pseudo-total and HCl-extractable 'bioavailable' fractions.

There are several methods and arguments to determine the concentration of metals bioavailable to aquatic organisms in sediment. Anthropogenically-sourced metals can bind to the heterogeneous geochemical phases of sediments in a variety of ways (Allen et al., 1993). These include those which are readily exchangeable, carbonate, hydrous ion, manganese oxide, organic matter, and sulphide forms. The strength with which heavy metals bind to these different phases determine a specific metals bioavailability (Tessier et al., 1979). A popular method for determining metal bioavailability in sediments is the Acid Volatile Sulphide - Simultaneously Extracted Metal (AVS-SEM) technique (Allen et al., 1993; Di Toro et al., 1990; McCready et al., 2003). This is based on the hypothesis that metals bound as sulphides are not bioavailable (McCready et al., 2003) and that AVS is likely important in determining metal toxicity in sediments (Di Toro et al., 1990). With this said, the Australian and New Zealand Environment Conservation Council (ANZECC) have a tiered decision tree approach to determining sediment quality, including the adoption of the two 'trigger value 'Interim Sediment Quality Guidelines (ISQG-low and ISQG-high). If the ISQG-low is exceeded, then factors which might lower the bioavailability must be examined (e.g. AVS, pore water concentration, organic carbon content and metal speciation). The ANZECC (2000) guidelines state that as a first level of screening, 1M HCl

extractable metal content should be adopted, as HCl does not break down the silicate mineral matrix (and thus release non-bioavailable metals) that would occur with a total metal digest using a strong acid (McCready et al., 2003). However, it is common in scientific investigations (including those previously in Christchurch and Haytons Stream) that recoverable (pseudo-total) metals in sediment are analysed and reported. Therefore, this thesis continued this trend in order to create comparable results with past results in the same city and catchment, as well as adopting the 1M HCl extraction, to simultaneously work alongside ANZECC recommendations and other local studies (McCready et al., 2003; Mills et al., 2012).

To extend knowledge from previous studies, the suite of trace elements analysed for was widened to include: aluminium (Al), arsenic (As), antimony (Sb), calcium (Ca), cadmium (Cd), copper (Cu), chromium (Cr), cobalt (Co), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), titanium (Ti), vanadium (V), and zinc (Zn).

2.2 Methods

2.2.1 Sampling site selection

Ten sites were selected in the catchment for sediment analysis (eight on Haytons Stream and two reference sites on the Heathcote River, upstream and downstream of the Heathcote-Haytons confluence). Sampling sites were chosen in consultation with Environment Canterbury staff, and for comparison with previous sampling sites along the stream where possible (Figure 2.1). Many of the sampling sites in the lower reaches of the stream were chosen due to the re-alignment (from the confluence of Haytons and Paparua Streams to Wigram Road), where sediment has not been sampled since re-alignment. Sites ranged from having ankle/ knee-deep water depths (0-50 cm at sites 1-3, 6 and 8) to deeper retention pools across the stream (≥ 1-1.5 metres at sites 4, 5 and 7) and were chosen to be spatially representative across the stream, as well as accounting for the industrial, pastoral and re-landscaped land-uses that Haytons Stream flows through. All sampling sites were visited prior to sampling, often accompanied by Environment Canterbury staff for discussion of suitability. Photographs of sampling sites are provided in Appendix 1.

In Figure 2.1 below, the sampling sites along Haytons Stream are outlined, where:

- Red points (sites 1-10) represent sediment and baseflow/ stormflow sampling sites for total and dissolved trace elements throughout the stream.
- Green points (sites 1, 3 and 7) represent where additional contaminant sampling took place (discussed in chapter three) for baseflow and stormflow sampling.
- The five red arrows are the locations of the water level and conductivity loggers throughout the catchment (discussed in chapter four).

A description of each site and specific sampling location is provided in Table 2.1, with sampled sites indicated with an x.

Table 2.1 Sampling and logger sites in this study

Site code	Description	Location	Sediment sampling	Water (metals) sampling	Additional sampling	Logger site
1. WAR	The first point where Haytons Stream becomes open channel	Waterloo Road	x	x	x	L2
2. GCP	Site of previous investigations	Gerald Connolly Place	x	x		
3. WBR	Re-emergence of Haytons into open channel	Washbournes Road	x	x	x	L4
4. LSA	Confluence of Haytons and Paparua streams	Lodestar Avenue	x	x		
5. TRW	Stream's new alignment	The Runway	x	x		
6. WGR	Bend in stream, location downstream of stormwater pipe from adjacent industrial land	Immediately above Wigram Road	x	x		L5
7. UWB	Before stream enters Wigram Retention Basin	Off O'Donnell Road	x	x	x	
8. DWB	After stream exits Wigram Retention Basin	Downstream of Wigram Retention Basin	x	x		
9. HEA-UHS	Upstream of the confluence with Haytons Stream	Heathcote River	x	x		
10. HEA-DHS	Downstream of confluence with Haytons Stream	Heathcote River	x	x		
Logger 1 (L1)	Stormwater manhole	Waterloo Road				L1
Logger 3 (L3)	Stormwater manhole	Springs Road				L3

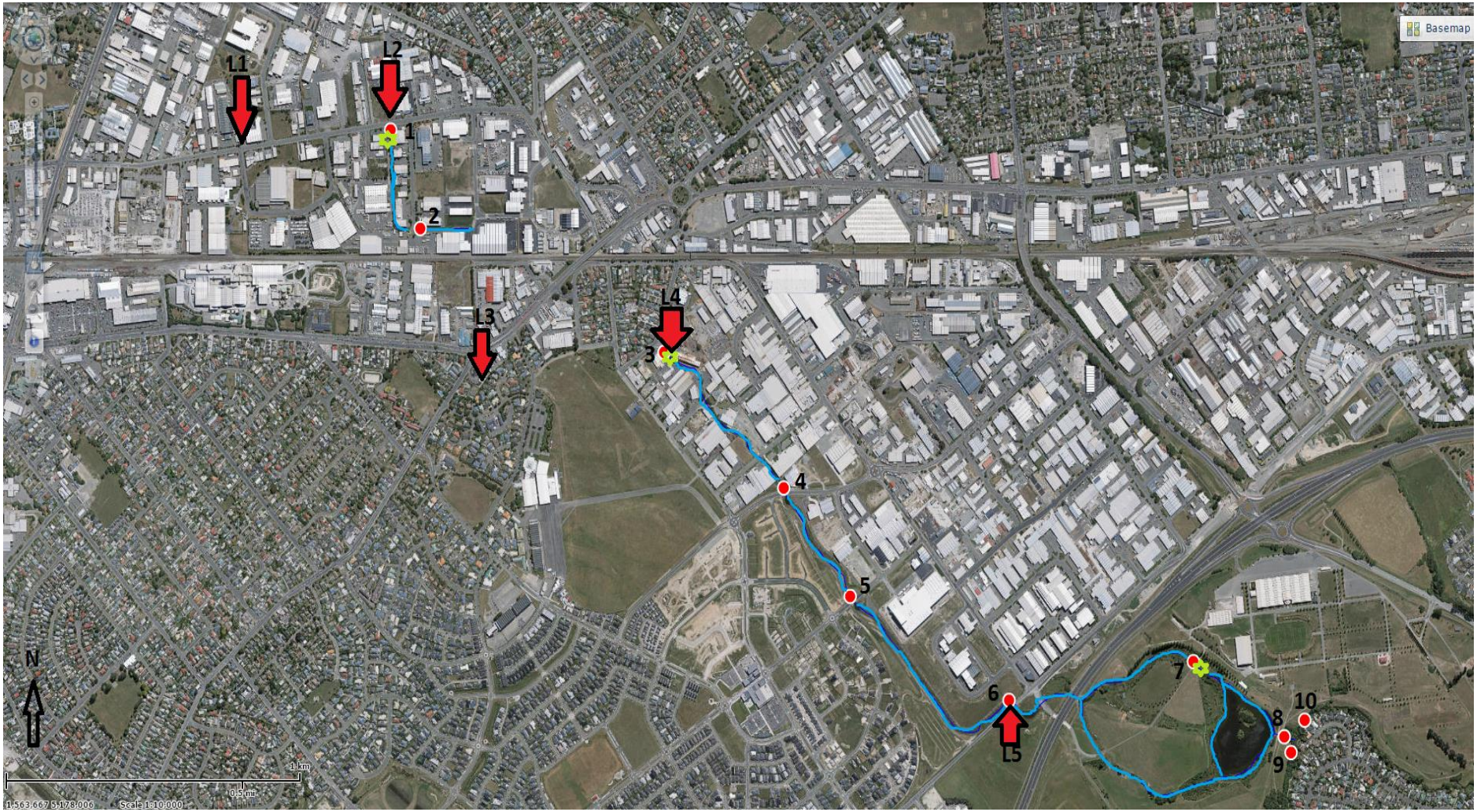


Figure 2.1 Sampling and logger sites across the Haytons Stream catchment (base image from canterburymaps.govt.nz)

2.2.2 Sediment collection

At each site a composite sediment sample was collected by scooping the top 2 cm of stream bed from multiple locations across the width of the site, using new 250 ml polystyrene containers. This sampling strategy was to ensure site heterogeneity was accounted for (United States Environmental Protection Agency, 2001), and that sufficient fine material was captured for analysis. Whilst the typical method of sediment collection is via coring, sediment sampling can be conducted with a spoon or scoop-material from beneath a shallow aqueous layer (0-12 inches in depth) if deemed necessary (United States Environmental Protection Agency, 2003). Past studies of the Haytons Stream bed sediments have adopted this approach, as the shallow depth of sediments to be collected and heterogeneous substrate make coring unfeasible (Moores et al., 2009). At shallower sites, new plastic spoons were used to scoop bed sediment, whereas at deeper sites a 'mighty gripper' sampling rod was used to drag the sampling container along the stream bed to capture fine sediment. Samples were labelled, zip-lock bagged, and stored on ice in a chilly bin before transport to the University of Canterbury. One site (WBR) was sampled twice, where a second sample was taken ~20 metres downstream, as the bed sediments changed composition substantially from cobble-pebble dominated to fine sand and silt-dominated.

2.2.3 Laboratory analysis

In the laboratory, sediment samples were placed in a drying oven at 70ºC for around six days, to remove moisture and destroy microorganisms in the samples. Each sample was thoroughly homogenized, before sieving to < 2mm.

Pseudo-total analysis

One gram of each sample was then placed into new 50 ml polycarbonate vials for acid digestion using a modification of US EPA 200.8. 4 ml of nitric acid (1+1) and 10 ml of hydrochloric acid (1+4) were added to each one gram of sample, which were then left to stand overnight to pre-digest. The samples were then heated in heating blocks at 85ºC for 10-15 minutes until the samples were seen refluxing. The samples were refluxed for a further 40 minutes before being cooled to room temperature. Samples were then made up to 20 ml with ultra-pure Milli-Q water and gently swirled to ensure mixing, and left again to stand overnight to settle particulates. Each sample was then diluted 21 times with 2% nitric acid for analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent 7500 Series ICP-MS with an octopole reaction system at the University of Canterbury.

Certified reference materials for sediment digestions (US National Institute of Standards and Technology Standard Reference Material 2702) and standard reference materials for the ICP-MS instrument (Standard Reference Material 1643f) were included in the digestion process, as well as

method blanks and sample duplicates to check for quality control. Sample detection limits, recoveries for blanks and recoveries for CRM's are presented in Table 2.2. For total sediment analysis, all duplicates were under 10% difference except for Al (10.68%) and As (10.34%). For bioavailable analysis, all duplicates were under 10% except for one Ni sample (11% difference).

Bioavailable analysis

'Bioavailable'/ labile metal fractions in the dried sediment samples were analysed via extraction with 1 M cold hydrochloric acid (Snape et al., 2004; Sutherland and Tack, 2008). Half a gram (0.5 g) of sediment from each site was weighed into new 50ml polycarbonate centrifuge tubes, and 50 ml of 1 M hydrochloric acid was added and the tubes placed on an end over end mixer overnight, for ~ 16 hours. Samples were then diluted 10 times with 2% nitric acid and sent for ICP-MS analysis.

Table 2.2 QA/QC data for sediment analysis

Pseudo-total metal digestion					Bioavailable metal extraction		
Element	Detection limits (µg/L)	CRM 2702 recovery %	ICP-MS CRM recovery %	Blanks (µg/L)	Detection limits (µg/L)	ICP-MS recovery %	Blanks (µg/L)
Mg	0.1	-	103	0.66	0.1	94.9	0.7
Al	10	5.42	109	<10	1	104	1.3
Ca	10	-	116	<10	100	99.9	<100
Ti	1	0.54	-	<1	1	-	<0.1
V	0.1	79	103	<0.1	0.1	103	0.2
Cr	10	77.1	89.8	<0.1	0.1	101	0.7
Mn	0.1	101	107	<0.1	0.1	94.1	0.1
Fe	0.1	15.6	105	3.89	1	111	4
Co	1	94.2	109	<0.1	0.1	90.9	<0.1
Ni	0.1	76.9	96.7	<0.1	1	104	<0.1
Cu	0.1	-	86.6	<0.1	0.1	97.3	<0.1
Zn	1	85.1	97.4	<1	0.1	108	1
As	1	94.4	104	<0.1	1	107	<0.1
Mo	1	-	108	<0.1	0.1	109	<0.1
Cd	0.1	103	105	<0.1	1	110	<1
Sb	0.1	10.7	103	<0.1	10	111	<10
Pb	0.1	96.6	95.6	<0.1	0.1	97.4	<0.1

Total Organic Carbon and Total Phosphorous

The remaining samples of dried sediment were sent to Hill Laboratories for analysis of Total Organic Carbon (TOC) and Total Phosphorous (TP) content. TOC was analysed through acid pre-treatment followed by catalytic combustion (900ºC, O_2), separation and thermal conductivity detection. Total Phosphorous was tested to compare with cadmium and instream nutrient concentrations in chapter three, to determine the spatial variability of nutrient contamination throughout the catchment, and was analysed via USEPA method 200.2 (nitric/ hydrochloric acid digestion and ICP-MS analysis).

2.2.4 Statistical analysis

Metal concentrations from the pseudo-total digest and bioavailable extraction were tested for correlations (and significance of correlations) and/ or any relationships present between each metal that exceeded a guideline. A Pearson correlation coefficient (in Microsoft Excel) was used to find any correlations between metals that exceeded ANZECC guidelines in sediment, and between pseudo-total and bioavailable concentrations of metals, which may assist in finding common/ similar sources. Due to the one-off sampling characterisation and low sample size, data was log-transformed to assume normality.

2.3 Results

2.3.1 Total Organic Carbon and Total Phosphorous in sediments

Total Phosphorous and Total Organic Carbon concentrations in sediment are shown in Figure 2.2 A&B below respectively. TP was relatively constant across the catchment, except for a large spike seen at site 3 (WBR 1 & 2- the same site and pattern as the sediment Cd spike). TOC was also similar at most sites, except at WBR and DWB, likely due to the stony substrate encountered at those locations.

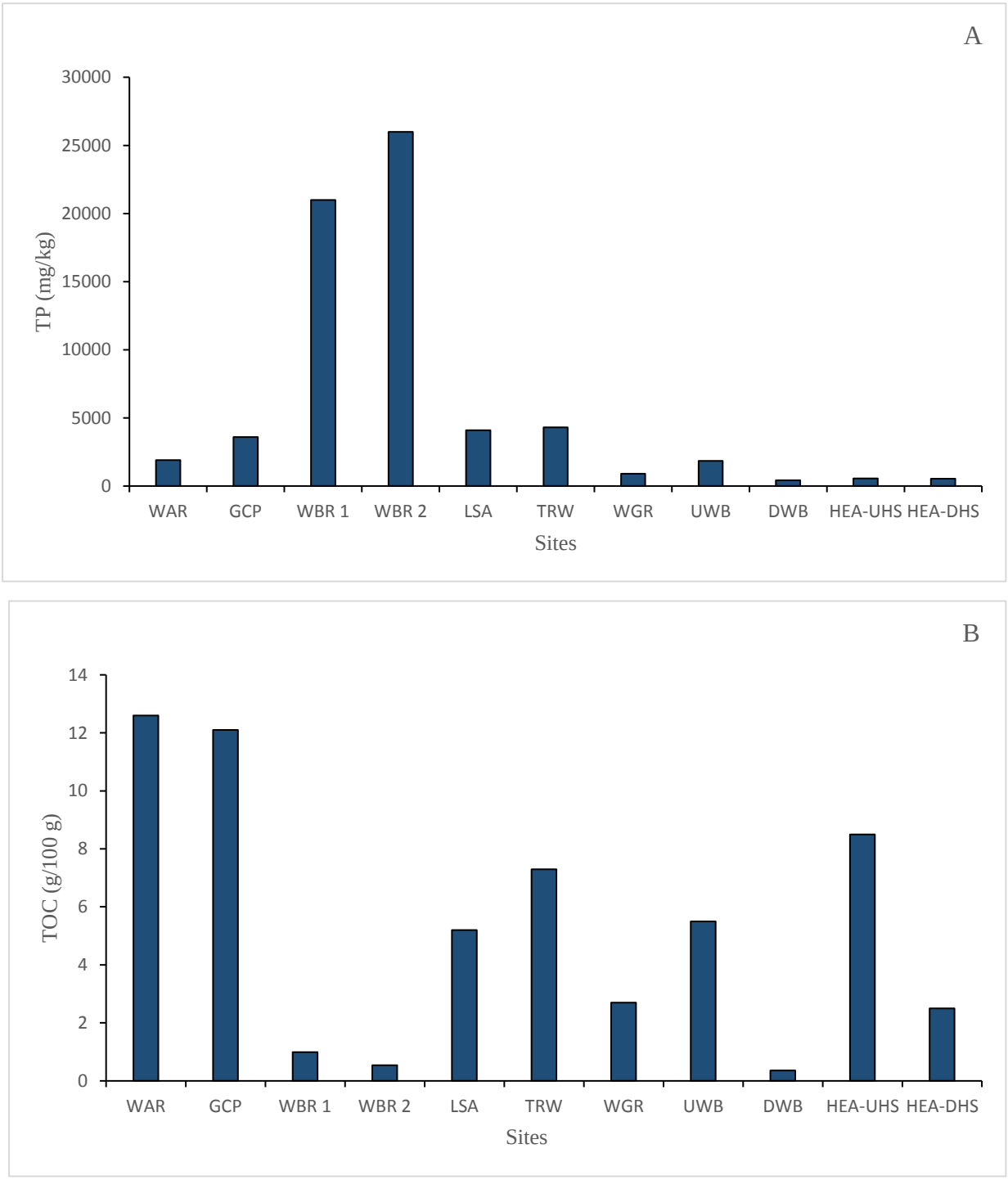


Figure 2.2 A) Total Recoverable Phosphorous, B) Total Organic Carbon in Haytons Stream sediment

2.3.2 Trace elements in sediments

Pseudo-total concentrations

The pseudo-total metals which exceeded ANZECC guidelines in the Haytons Stream catchment are presented below in Table 2.3. The metals that exceeded ANZECC guidelines for pseudo-total metals at least at one site were Ni, Cu, Zn, Cd, Sb and Pb (Table 2.3 and Figure 2.3). The full dataset of pseudo-total and bioavailable metals in sediment is provided in Appendix 2.

Table 2.3 Pseudo-total metals exceeding ANZECC guidelines in Haytons Stream sediments

Elements	Ni	Cu	Zn	Cd	Sb	Pb
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
ANZECC ISQG-low	21	65	200	1.5	2	50
ANZECC ISQG-high	52	270	410	10	25	220
Sites						
WAR	23.7	149	3455	1.16	2.54	184
GCP	26.6	144	3466	1.48	3.28	121
WBR 1	13.2	54.9	877	6.16	0.61	79.7
WBR 2	17.9	33.9	2245	8.28	0.55	115
LSA	16.6	68.9	2568	1.9	1.71	121
TRW	21.3	96.9	2976	1.9	1.59	126
WGR	14.9	44	978	0.39	0.58	48.9
UWB	15.7	59.6	1839	1.72	0.62	120
DWB	7.94	5.95	218	0.18	0.07	8.99
HEA-UHS	10.8	30.2	351	0.86	0.27	83.4
HEA-DHS	9.69	19.4	1032	0.81	0.26	42.2[1]

[1] Yellow-highlighted concentrations exceed the respective ISQG-low, red-highlighted concentrations exceed the respective ISQG-high guideline.

Antimony

Sb concentrations exceeded guideline levels at the first two sites of WAR and GCP, where concentrations were 2.54 and 3.28 mg/kg respectively (above the 2 mg/kg ANZECC ISQG-low). At all other sites, Sb was below the ANZECC ISQG-low.

Cadmium

Five of the ten sampled sites exceeded the ISQG-low guideline for Cd, tending to be in the middle-lower section of the catchment, and all on Haytons Stream. These sites were WBR 1 and 2, LSA, TRW and UWB. WBR site 2 contained the highest Cd concentration of 8.28 mg/kg. WBR site 1 was also elevated compared to other sites, with a concentration of 6.16 mg/kg.

Copper

The ANZECC ISQG-low guidelines for copper were exceeded at four sites on Haytons Stream, being WAR, GCP, LSA and TRW. The highest concentration was 149 mg/kg at WAR, with GCP having a comparable concentration of 144 mg/kg.

Lead

All sites on Haytons Stream exceeded the ISQG-low for Pb, except for WGR and DWB. All other sites were elevated, with the highest at WAR with a concentration of 184 mg/kg compared to an ANZECC low guideline of 50 mg/kg.

Nickel

The two sites with highest concentrations of nickel in Haytons Stream were the first two sampling sites of WAR and GCP, with concentrations of 23.7 and 26.6 mg/kg respectively. All other sites were below the ANZECC ISQG-low of 21 mg/kg of Ni, except for TRW which had a Ni concentration of 21.3 mg/kg.

Zinc

The ANZECC ISQG-high guideline of 410 mg/kg was exceeded at every site on Haytons Stream except for downstream of the Wigram Retention Basin (DWB), where the ISQG-low was exceeded. This may be due to the coarse nature of substrate present at this site and greater difficulty encountered in capturing fine material < 2mm, and not necessarily a reflection of less contamination. The highest concentration found in Haytons Stream was at GCP, significantly above the ISQG-high at 3466 mg/kg. Waterloo Road sediment was similar in concentration, at 3455 mg/kg. On the Heathcote River, the ISQG-low was exceeded above the confluence with Haytons Stream, where downstream of the confluence the concentration near-tripled to 1032 mg/kg.

Of all pseudo-total metals exceeding a guideline, the first two sampling sites (WAR and GCP) typically held the highest concentrations, which dropped off yet remained elevated in other the industrial sites (WBR-TRW) of the catchment. The industrial sites tended to have higher concentrations than the sites in the lower pastoral section, near and around the Wigram Retention Basin and Heathcote River (Table 2.3).

Bioavailable concentrations

Bioavailable metals extracted through the cold HCl extraction were then compared to the previous pseudo-total concentrations which exceeded a guideline (Table 2.4 and Figure 2.3).

Table 2.4 Bioavailable metal concentrations measured using an HCL extraction

Elements	Ni	Cu	Zn	Cd	Pb
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Sites					
WAR	12.3	92.3	3850	0.96	146
GCP	13.2	81.6	3685	1.25	96.9
WBR 1	5.58	22.0	1327	9.98	47.8
WBR 2	5.42	13.2	2229	5.73	127
LSA	6.44	39.0	2879	1.66	100
TRW	8.09	78.7	3822	2.04	126
WGR	5.99	28.8	1113	0.38	39.5
UWB	3.83	29.8	1846	0.19	107
DWB	1.36	4.67	218	0.19	8.32
HEA-UHS	3.09	15.6	238	0.72	57.8
HEA-DHS	2.55	12.2	1010	0.79	34.3

Cadmium

Homogeneity issues were observed in bioavailable cadmium concentrations. Although there were widespread decreases in concentration, two sites (WBR 1 and TRW) increased in concentration. At WBR, the substrate was substantially stony and coarse, with large sections of the bed littered with unidentified yellow chemical residue and other chemical by-products. As a sample was taken in composite across the width of a site, each lab analysis aliquot may pick up something in the sediment the previous did not (for example a high concentration chemical pellet), and therefore higher Cd concentrations might have shown in the HCl extraction. The two highest concentrations of cadmium were at WBR 1 and WBR 2 (9.98 and 5.73 mg/kg respectively). Bioavailable cadmium extraction percentages ranged from 11- 162%, with an average of 90%.

Copper

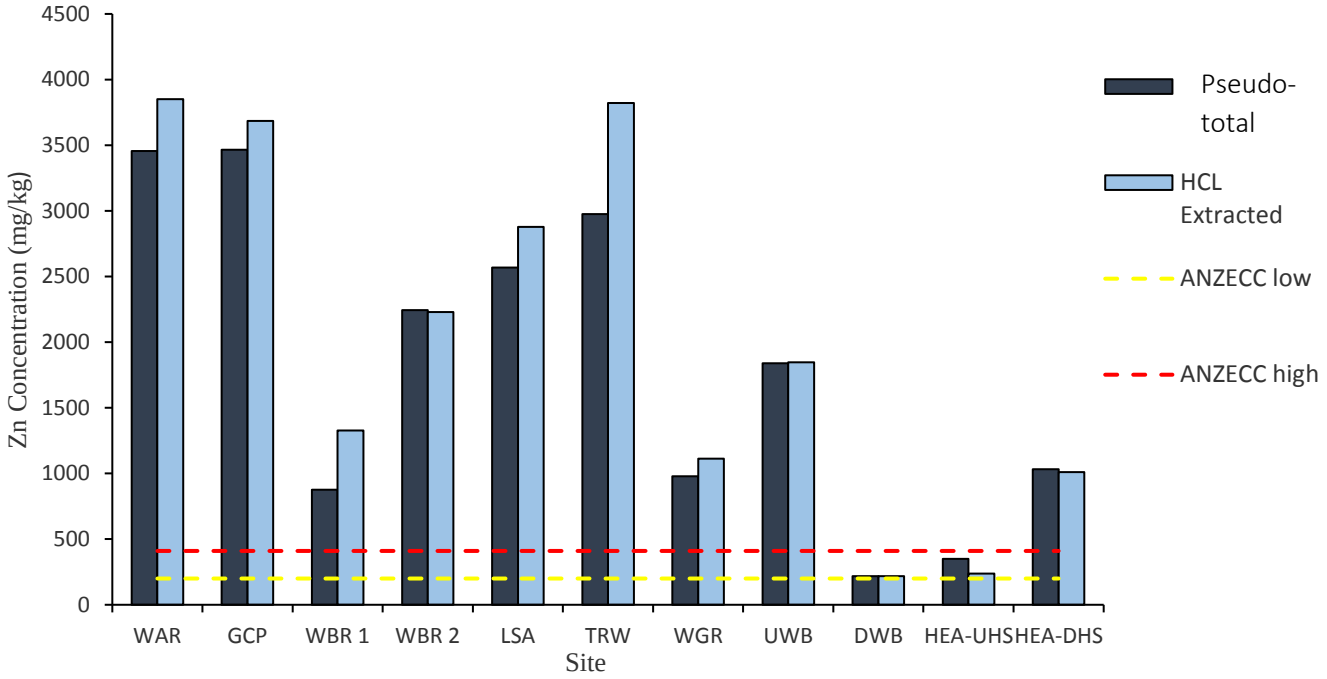
The HCL-extractable copper concentrations were lower than the pseudo-total concentrations at all sites, yet the same patterns of the first two sites of WAR and GCP having the highest concentrations of 92.3 and 81.6 mg/kg respectively remained. Copper extractions were much lower, ranging from 39-81% with an average of 59% bioavailability.

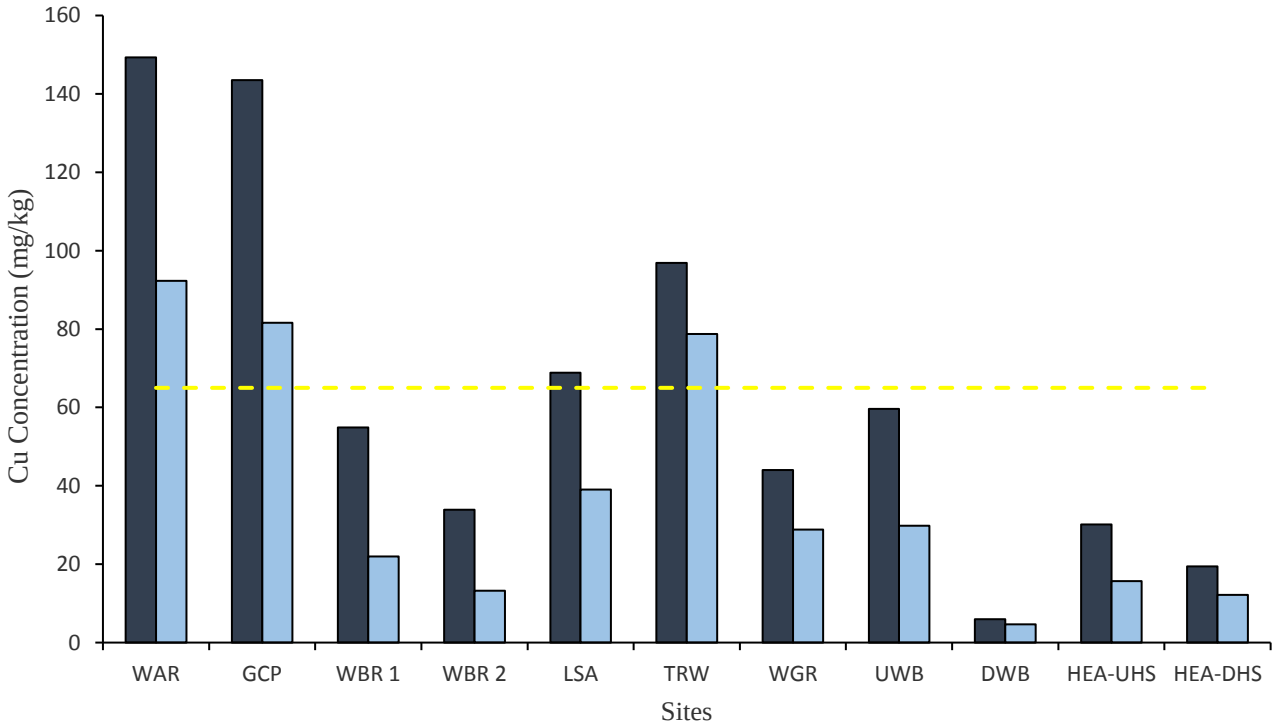
Lead

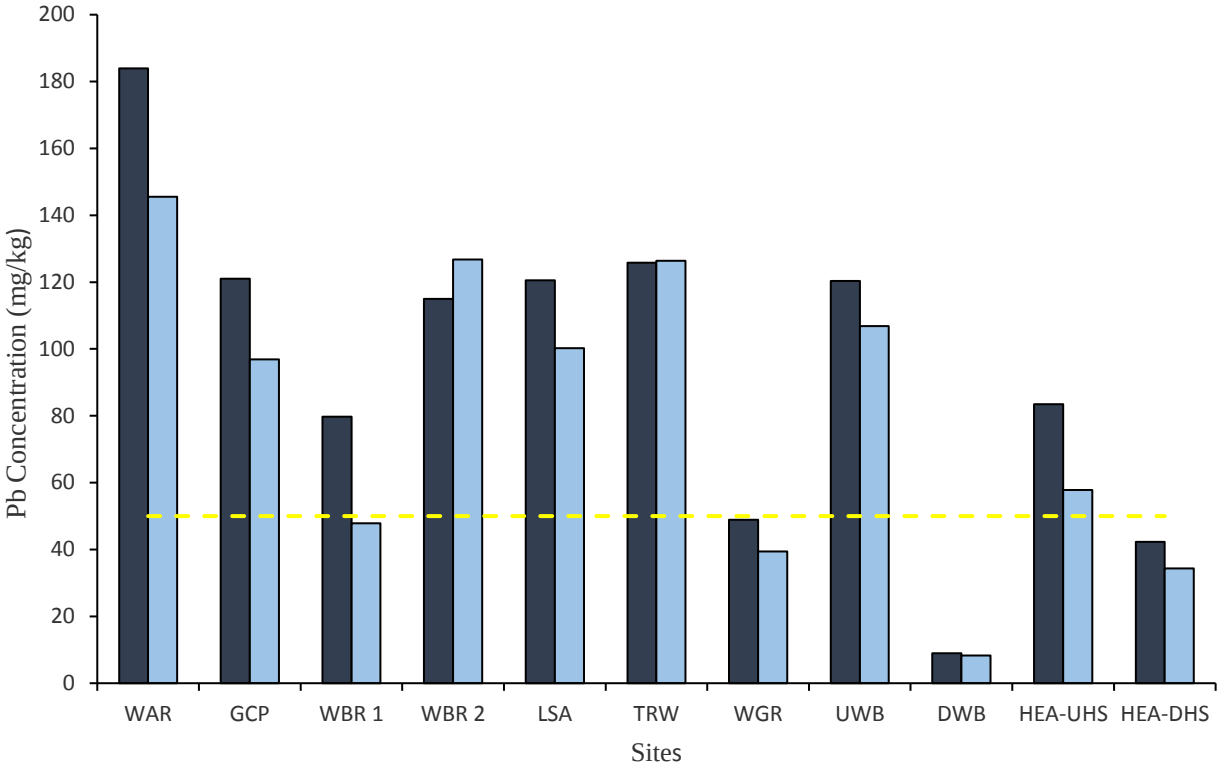
Every site decreased in Pb concentration after the bioavailable extraction, except for WBR 2 and TRW, further suggesting a homogeneity issue in the sediment. Although all other sites decreased, there were still seven sites where bioavailable Pb exceeded the ISQG-low guideline of 50 mg/kg (with six of those on Haytons Stream). The two highest sites were the same as the pseudo-total digests, being WAR and GCP (146 and 96.9 mg/kg respectively). Bioavailable Pb extractions ranged from 60- 110%, with an average of 84%.

Zinc

The bioavailable extraction produced similar if not higher zinc concentrations in sediment when compared to the recoverable digests. The same homogeneity issues in the sediment were therefore likely seen for Zn, as some sites are very coarse in substrate whilst some remain very fine and silt-dominant. The presence of particulate zinc in the sediment was also not quantified across the sites, which may be a particular issue in this industrial catchment. Concentrations remained very high in zinc after the HCl extraction, with most sites increasing or remaining at similar concentrations. The highest concentration of labile Zn was found at WAR, at 3850 mg/kg. Bioavailable zinc extraction percentages were high, ranging from 68- 151% (with an average of 108%). On Figure 2.3 below, the pseudo-total and bioavailable results for Zn, Cu, Pb, Cd, Sb and Ni are presented respectively.


4500
4000
3500
3000
2500
2000
1500
1000
500
0
Zn Concentration (mg/kg)
WAR
GCP
WBR 1
WBR 2
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site
Pseudo-total
HCL Extracted
ANZECC low
ANZECC high


160
140
120
100
80
60
40
20
0
Cu Concentration (mg/kg)
WAR
GCP
WBR 1
WBR 2
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Sites


200
180
160
140
120
100
80
60
40
20
0
Pb Concentration (mg/kg)
WAR
GCP
WBR 1
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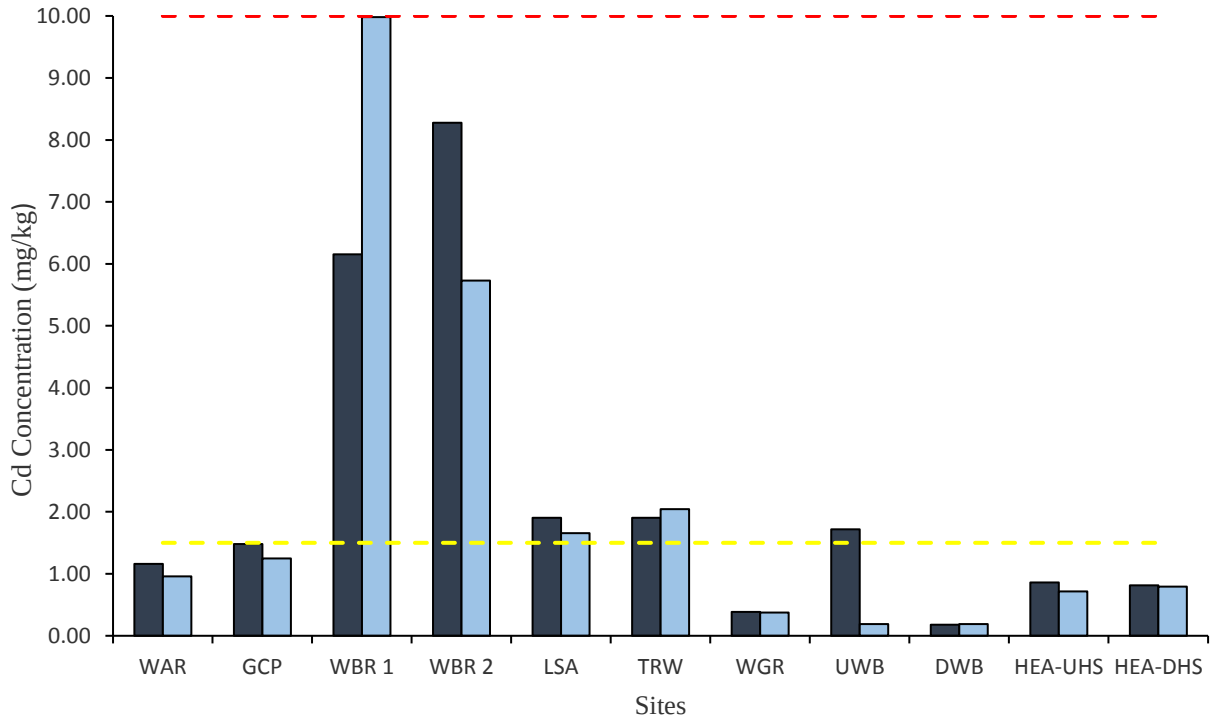
HEA-UHS
HEA-DHS
Sites


10.00
9.00
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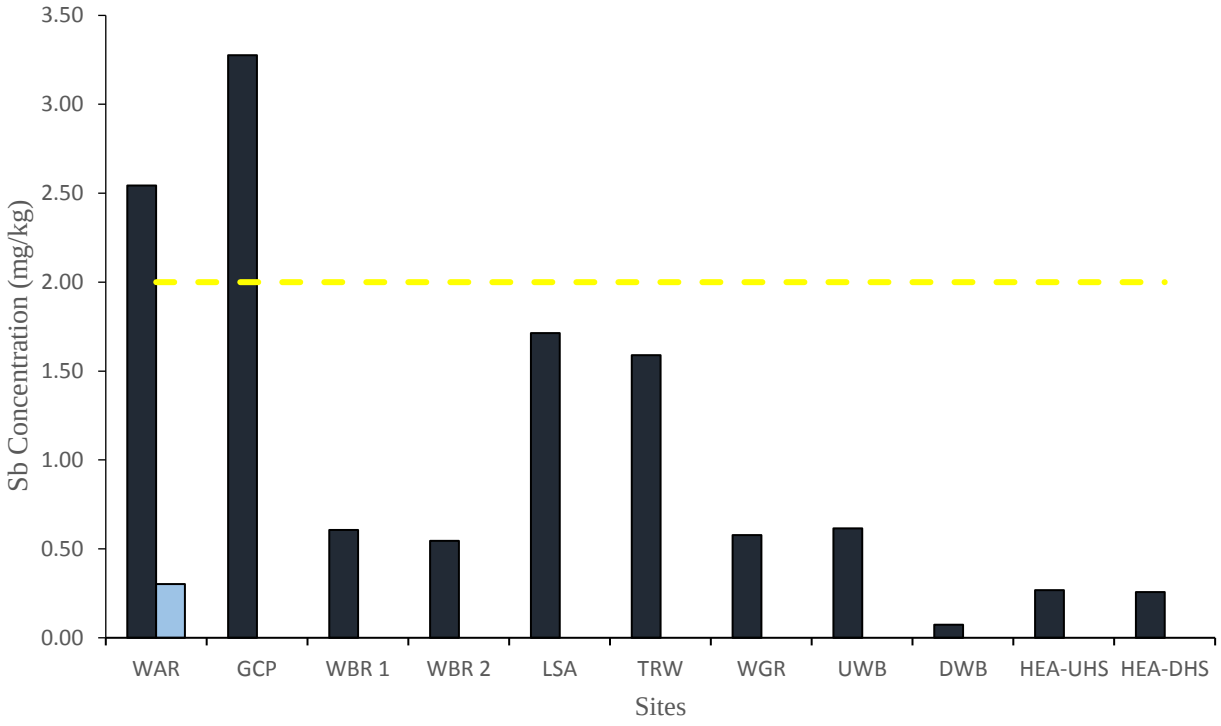
Cd Concentration (mg/kg)
WAR
GCP
WBR 1
WBR 2
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Sites



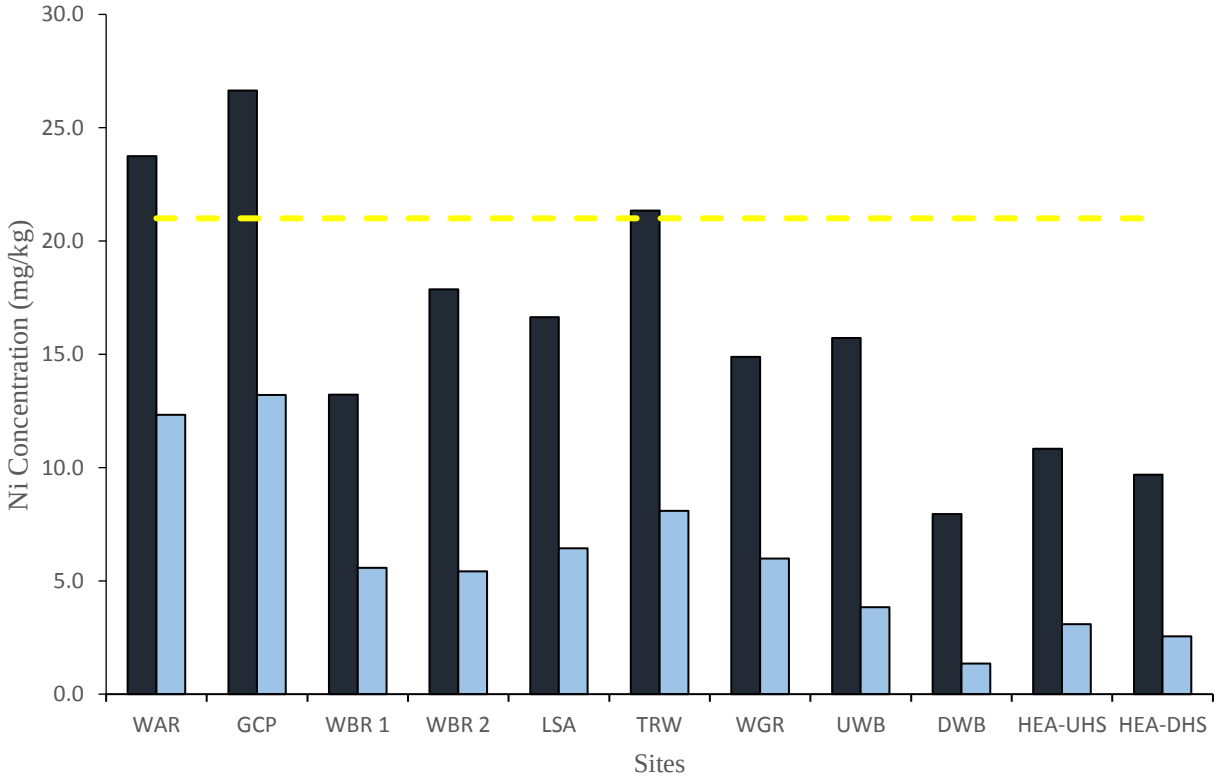


Figure 2.3 Pseudo-total and HCl extracted metals in Haytons Stream sediment

2.3.3 Comparison of recoverable and extracted metals

The extraction percentage/ amount of metals extracted using the bioavailable HCl extraction was compared to the concentrations of the pseudo-total metal digest (Figure 2.4).

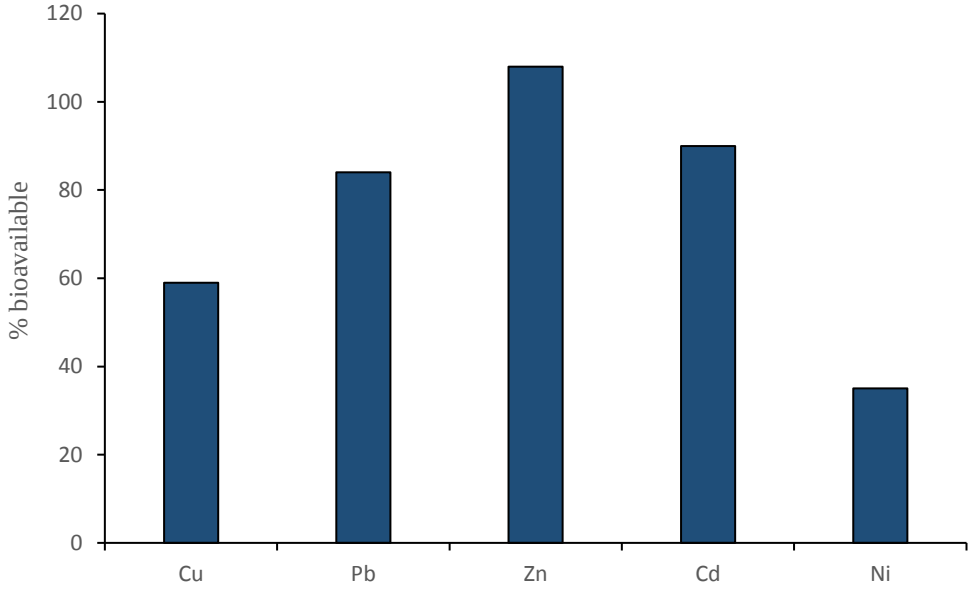


Figure 2.4 Average percentage metal extraction for guideline-exceeding metals

As described, the metals Zn, Cd and Pb had high bioavailability seen through the high extraction percentages, with these three metals having average extraction percentages of over 80% (Zn and Cd were particularly high at over 90% average extraction). Percentage of nickel extraction were the lowest of all guideline-exceeding metals, ranging from 17- 52% (average of 35%), meaning that Ni was the least bioavailable of the metals that originally exceeded the pseudo-total guidelines.

From these generally high bioavailable extraction percentages from the weak acid leach, it can be concluded that (at least for the above metals), a significant portion of guideline-exceeding metals present in the Haytons Stream catchment are in a labile (and potentially readily-bioavailable) state (i.e. easily removable from the sediment).

Correlations between contaminants

The results of Pearson's correlation coefficients, which were calculated between pseudo-total and HCl extracted concentrations, between different metals, and between TOC and TP are presented in Table 2.5. Yellow-highlighted boxes indicate strong positive correlations (i.e. increases in concentration strongly together across the catchment), with stars denoting correlations of statistical significance. Many metals increased in concentration together across the catchment, indicating similar sources, particularly for Zn, Cu, Ni and Pb. TP strongly correlated with Cd (0.92 and 0.85 for total/ bioavailable concentrations), yet not for other metals (Table 2.5). There were also strong correlations between TOC in sediment and pseudo-total/ bioavailable copper, and for pseudo-total antimony. This can be explained by the higher TOC concentrations at the first two sampling sites (Figure 2.2), which also held higher concentrations of Cu and Sb in sediment.

Table 2.5 Pearson product moment correlation coefficients for metals in sediment (yellow boxes indicate strong correlations)

Same metal	Correlation [2]	Between metals	Correlation (recoverable digest)	Correlation (HCl extraction)	Metals- TOC/TP	TOC Correlation Tot/Bio metals	TP Correlation Tot/Bio metals
Tot Zn – Bio Zn	0.99***	Zn – Cu	0.91***	0.89***	Tot/Bio Zn	0.78**/ 0.77**	0.54/ 0.59*
Tot Cu – Bio Cu	0.96***	Zn – Pb	0.95***	0.96***	Tot/Bio Cu	0.87***/ 0.94***	0.45/ 0.29
Tot Pb – Bio Pb	0.98***	Zn – Cd	0.54	0.44	Tot/Bio Pb	0.70**/ 0.67*	0.54/ 0.55
Tot Cd – Bio Cd	0.84***	Zn – Ni	0.96***	0.91***	Tot/Bio Cd	0.01/ -0.12	0.92***/ 0.85***
Tot Ni – Bio Ni	0.95***	Cu – Pb	0.91***	0.77**	Tot/Bio Ni	0.80**/ 0.77**	0.52/ 0.52
		Cu – Cd	0.44	0.18	Tot/Bio Sb	0.87***/ n/a[3]	0.47/ n/a
		Cu – Ni	0.93***	0.92***			
		Pb – Cd	0.69	0.41			
		Pb – Ni	0.88***	0.80**			
		Cd – Ni	0.43	0.44			

[2] * $p < 0.05$
** $p < 0.01$
*** $p < 0.001$

[3] Bioavailable antimony concentrations mostly below detection limits; unable to analyse data.

Site ranking/ hazard quotient

Pseudo-total trace element concentrations were divided by their relevant ANZECC ISQG-high guideline, and all metal ratios for each site added together to create a 'hazard quotient' to identify the worst site for trace element hazard in sediment. This better illustrates which sites are the poorest quality and harbour the highest potential exposure in Haytons Stream (Table 2.6). In this, ratios above 1 highlight that adverse effects are possible (i.e. concentration higher than guideline), whereas if they are below 1 they are unlikely. The first two sites in the catchment (WAR and GCP) had the highest hazard quotient, which could be expected as these two sites generally held the highest metal concentrations in sediment.

Table 2.6 Hazard quotient for trace elements in sediment for each sampling site

Site	Hazard quotient
WAR	10.8
GCP	10.7
WBR 1	3.76
WBR 2	7.50
LSA	7.91
TRW	9.17
WGR	3.29
UWB	5.94
DWB	0.83
HEA-UHS	1.84
HEA-DHS	3.19

2.4 Discussion

Total (pseudo-total) metal concentrations

Elevated concentrations of numerous metals (particularly Zn, Cu, Pb and Cd) were measured throughout the length of Haytons Stream sediment. Concentrations of Zn were highly elevated at all sampled sites throughout the length of the waterway. Previous studies in Christchurch and throughout New Zealand have found that Zn (and other metals) are of environmental concern in urban stream bed sediments, however Haytons Stream in this study exceeds other local published or reported concentration data (Table 2.7). For example, Blakely and Harding (2005) found in Okeover Stream in Christchurch, maximum sediment concentrations of 332, 180 and 200 mg/kg Zn, Pb and Cu respectively.

Haytons Stream can be compared to the Okeover, as they both receive direct stormwater discharges and drain urban areas of Christchurch. Research from the Okeover Stream does not reflect well for Haytons Stream, given that restoration efforts to improve habitat and flow conditions, riparian planting and shading in Okeover are not being met with increased instream ecology; likely due to the continual presence of ecologically toxic metal concentrations throughout the stream bed and water column (Blakely and Harding, 2005; O'Sullivan et al., 2012). The concentrations found in sediment along Haytons Stream in this study are far beyond those reported by Blakely and Harding (2005) and O'Sullivan et al. (2012) in the Okeover, or in other Christchurch catchments (Table 2.7).

Table 2.7 Maximum sediment concentrations in this study compared to other Christchurch catchments

Maximum sediment concentrations (mg/kg)	Blakely and Harding (2005)	O'Sullivan et al. (2012)	Gadd and Skyes (2014)	Gadd (2015)	Moores et al. (2009)	**This study**
	(Okeover)	(Okeover)	(Avon)	(Heathcote)	(Haytons)	(Haytons)
Copper	200	82 ± 60	78	39	16	149
Lead	180	199 ± 442	780	136	41	184
Zinc	332	677 ± 196	770	450	450	3850
Cadmium	0.26	-	0.57	0.39	-	9.98
Total Phosphorous	-	-	2400	890	900	26,000

Haytons Stream sediment has concentrations of certain metals that are both comparable to other catchments (lead), elevated compared to other catchments (copper) and significantly contaminated compared to other Christchurch catchments (zinc and cadmium). Sediment cadmium concentrations in

the mid catchment of Haytons were far in exceedance of any other local published data, with the highest site in this study (WBR) 21 times higher than the highest on the Heathcote (Gadd, 2015), and 14.5 times higher than that on the Avon (Gadd and Skyes, 2014). The concentrations of cadmium measured at this site on Haytons Stream are comparable to international concentrations caused by domestic, mixed and industrial effluents. Concentrations between 5-10 mg/kg are commonly sourced from communal wastewater effluents with an occasional industrial presence, for example from the electroplating industry (Förstner, 1984). Industries which may be sources of cadmium pollution are present in the Haytons catchment, and may need further investigation. When compared to 42 urban waterways in Wellington, New Zealand (Milne and Keenan, 2008), Haytons Stream shows a similar pattern of having substantially higher concentrations of metals that commonly exceed guidelines (Cu and Zn). All concentrations of zinc and copper were higher in Haytons, with similar concentrations in nickel and occasionally antimony between Haytons and Wellington urban streams.

Comparison of this research with past Haytons Stream data is of further ecological concern. When comparing historical monitoring in Haytons Stream to this study (Table 2.7), Cu, Pb and Zn have all increased in concentration at identical sampling sites (Wigram Road, confluence of Haytons and Paparua Streams, upstream of the WRB) (Christoffel, 1995; Kingett Mitchell, 2005). Moores et al. (2009) provided perhaps the best comparative study for how Haytons Stream sediments have changed through time; who surveyed Gerald Connolly Place and upstream/ downstream of the WRB. When comparing this, most metals and sites have increased in concentration (particularly Cu, Pb and Cd), whilst some (specifically Zn) have substantially increased in concentration. Globally, these sediment concentrations are comparable with what has been reported elsewhere in industrial and heavily urbanised areas, particularly for Cu and Pb, whilst Zn concentrations in this study in Haytons Stream still remain highly elevated in comparison to other industrial catchments (Kim et al., 1998; Pekey, 2006; Sekabira et al., 2010). The concentrations found in this study are also substantially elevated beyond those reported to alter and degrade microcosm macroinvertebrate communities in urban streams in Australia (Marshall et al., 2010).

Total Phosphorous (TP) concentrations in sediment follow the profile of Cd, corroborated by strong positive Pearson correlations at WBR, with large spikes of both of these contaminants present at this site. TP concentrations throughout all of Haytons Stream were elevated compared to the recent reported range of 310-890 mg/kg in the Heathcote River catchment (Gadd, 2015), with most sites on Haytons Stream comparable to the 1000-2400 mg/kg reported in Riccarton and Addington Drains in Christchurch (Gadd & Skyes, 2014). There is no relevant guideline for nutrients in sediments (ANZECC, 2000), yet it is clear that Haytons Stream is elevated in TP beyond most Christchurch catchments, and site three has concentrations suggesting clear anthropogenic contamination, suggesting substantial phosphorous and cadmium pollution is occurring between sites 2 & 3. Similar occurrences

of elevated phosphorous (DRP) and other nutrients have been found between these two sites in previous Haytons Stream investigations, within the reticulated stormwater network (Moores et al., 2009).

Potential bioavailability of trace elements

The results of this research that some HCl-extracted metals (especially Zn and Cd) are similar in concentration to the recoverable metals, are of significant ecological concern. This suggests that these metals in Haytons Stream sediments are labile at high concentrations, and could be a significant source to the overlying water column, due to their ease of release. This study corroborates other similar research in that the HCl method may not necessarily relate to absolute bioavailability in sediment, due to the high extraction percentages seen (McCready et al., 2003; Sutherland and Tack, 2008). However, the HCl extraction provides a quick, cheap and simple method for determining labile metal concentrations in sediment which can then be analysed and interpreted as a reasonable approximation of what metals are at ecologically-concerning concentrations. After this, information can then be generated to determine or target specific areas/ sites for more detailed investigation to determine a more definitive metal bioavailability, which incorporates biota and/ or sulphide content of the sediment at each specific location (Snape et al., 2004).

In the case of this study, the HCl-extracted concentrations have highlighted the metals of highest immediate ecological concern and highest bioavailability in Haytons Stream (e.g. Zn and Cd, compared to Zn, Cu, Pb, Ni, Cd and Sb for pseudo-total metals). This method has also highlighted and further delineated the specific locations where labile metal concentrations are highest, indicating the sites which are of greatest concern and hazard for ecological and sediment quality (upper and middle industrial sections of the stream).

Implications of bioavailable concentrations to the aquatic ecosystem and metal mobilisation

If Haytons Stream is to ever improve ecologically, exposure of aquatic organisms to elevated trace element concentrations needs to be addressed. It is likely that these metals in sediment are hampering any substantial ecological activity in Haytons Stream, and will continue to do so unless remedial action is taken. Metals in sediment have been observed to damage aquatic organism health, regardless of chemical speciation (Lee et al., 2000). If benthic-feeding invertebrates cannot establish or survive due to elevated metal concentrations in sediments, then a sustainable and diverse freshwater ecosystem cannot be expected in Haytons Stream or elsewhere. Moreover, many of the EPT taxa that represent a clean and unpolluted waterbody ingest detritus or periphyton to some degree (Smock, 1983), implying that their presence in Haytons Stream will be continually limited by the high metal concentrations across the catchment's sediment.

Chapman et al. (1998) stated that the only reliable way to proactively measure the true bioavailability of metals in sediment is to perform bioassays, or by reactively assessing the community structure

present relative to contamination. In the case of Haytons Stream, the severely depauperate ecological community seen in the catchment (McMurtie, 2002) is likely a result of the high metal concentrations present in sediment, other contaminant bioavailability's, as well as mud-smothered stream substrates. The lack of any substantial ecological community structure throughout Haytons Stream provides clear evidence that contaminants are bioavailable to any aquatic organisms previously or currently present.

Contaminants in sediment can become redistributed in the water column or made bioavailable with sediment disturbance events (Eggleton and Thomas, 2004). These events, whether natural (such as storms) or anthropogenic (such as dredging, fishing or through disposal) can result in modifications of chemical properties in the sediment and thus remobilise contaminants and increase bioavailability (Eggleton and Thomas, 2004). As metals commonly bind to metal sulphides under anoxic conditions (Di Toro et al., 1990), a substantial enough disturbance event can lead to exposure of anoxic sediments to oxic conditions, resulting in changes to the dissolved oxygen, redox potential, and thus release of metals to the overlying water column, primarily through mobilisation and transfer of metals from sulphide-bound complexes (Calmano et al., 1993; Eggleton and Thomas, 2004).

Implications for metal sources and historical/ legacy contamination

For every metal that exceeded a guideline in sediment, the two locations of highest concentration were consistently the first two sites of Waterloo Road and Gerald Connolly Place (with the exception of Cd, which peaked at Washbournes Road). This was also the case for metals that did not exceed guidelines or those which have no guidelines; for example, Cr, Mn, Mo and Co (data in Appendix 2). These sites had high if not the highest recoverable metal concentrations across many analysed metals, which fluctuated concentrations down the catchment. These two sites also had the highest hazard quotients in sediment relative to ANZECC guidelines, suggesting that they are the worst sites in the catchment for both sediment quality and ecological hazard. The site at Waterloo Road was immediately after the stream exits from the stormwater network, creating a slow-flowing pool of water before the stream narrows out and begins its flow to Gerald Connolly Place. As the stream immediately drains the stormwater network into this body of water, some sediment and solids may immediately drop out of the water column, resulting in the thick silty-mud substrate found at Waterloo Road. As the stream narrows and flow picks up, the substrate changes to more cobble and course-particle dominated (Figure 2.5- where stars indicate this study's sites). This thick silt deposit may partially explain the elevated metal concentrations found at Waterloo Road, due to metals preferentially binding to finer-sized particles with higher surface areas (Horowitz and Elrick, 1987; Zanders, 2005). The first two sites are also disconnected from the rest of the catchment, as the stream re-enters the stormwater network between GCP and WBR. This disconnection in the stream after the first two sites, which are likely sediment and contaminant sinks for industrial activity in the upper catchment, is perhaps another reason why WAR and GCP consistently have the highest concentrations for a range of metals in sediment.

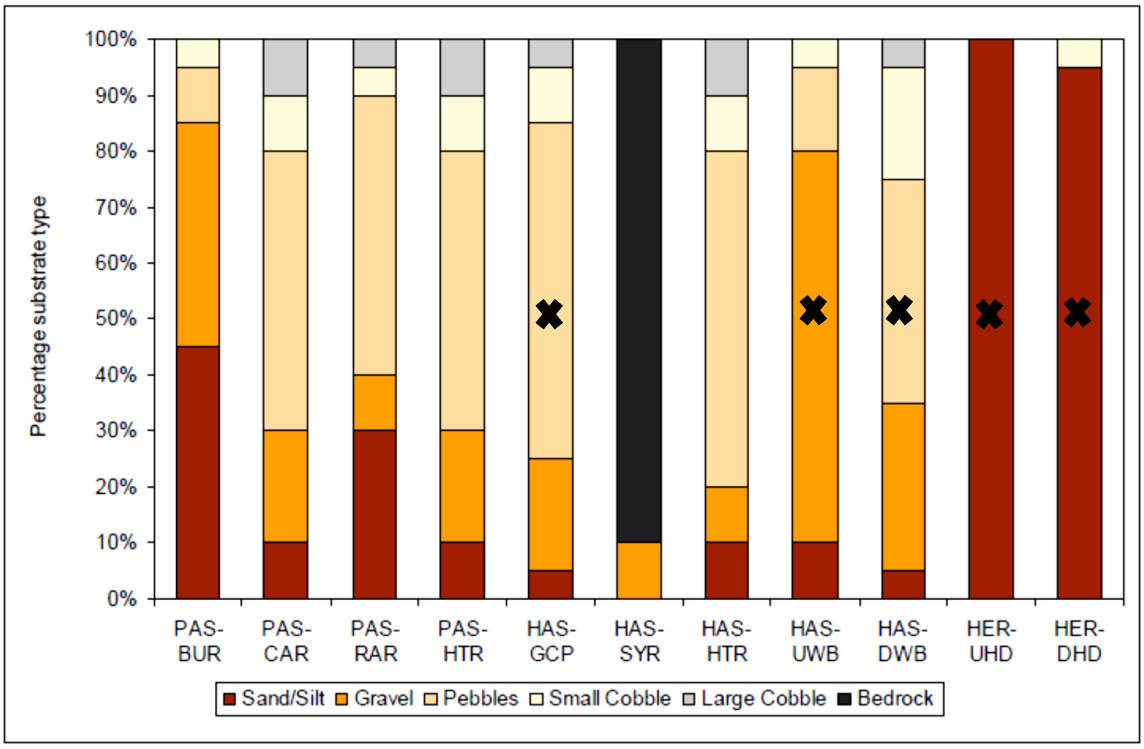


Figure 2.5 Previous visual assessment of Haytons/Paparua Stream bed sediments (Moores et al., 2009)

Many metals increased in concentration together on average across Haytons Stream (Table 2.5), with strong positive correlations between Zn and Cu, Zn and Ni, Cu and Ni, and Zn and Pb indicating a similar source. These four metals all have similar anthropogenic sources, predominantly from road dust and vehicle engine, exhaust, brake and tyre wear, and have been reported to positively correlate with each other (Davis et al., 2001; Sutherland, 2000). It is therefore likely that these metals in sediment all originate from similar sources in this highly industrial catchment, such as those stated above. Additionally, TOC and total/ bioavailable metal correlations suggest that Cu binds strongly to organic matter in sediment (strong positive correlation values of 0.87 and 0.94), which is corroborated when considering the sites with consistently highest metals concentrations (WAR and GCP) also had the two highest TOC concentrations of 12.6 and 12.1 g/100 g respectively. The same correlations (particularly copper) and implications for metals complexing onto sediments with high TOC contents have been found elsewhere (Seidemann, 1991; Wang et al., 2004).

A local study of metal sources in urban industrial areas in Auckland, New Zealand concluded that there are abundant metal sources present in industrial land use areas (Table 2.8).

Table 2.8 Industrial sources of copper, lead and zinc (Kennedy and Sutherland, 2008)

Land use	Generic source	Principal source	Zinc source	Copper source	Lead source
	Wet and dry deposition from air emissions	Emissions from local industry	Y	Y	Y
Industrial buildings	Building facades	Paints	Y	Y	Y
		Exposed architectural material	Y	Y	Y
		Glass	Y	UL	UL
		Plastic and other facings			
	Building roofs	Metal roofing products	Y	Y	Y
		Metal gutters	Y	Y	UL
		Metal flashings	UL	UL	Y
		Roofing paints	Y	Y	Y
		Atmospheric deposition	Y	Y	Y
		Roofing biocides	Y	Y	UL
Other	Industrial site runoff	Onsite activities leading to contamination and runoff	P	P	P
	Spills		P	P	P
	Metal traffic lights		Y	UL	UL

Note: Y= yes, P= possible, UL= unlikely

From the above table, there is a large variety of metal sources present in industrial areas, essentially all of which are present throughout the Haytons Stream catchment. Whilst in the field, the catchment was also seen to hold other metal-using industries, including galvanising, truck repairs and the abundant presence of large 18-wheeled transportation trucks. In this study, zinc was found at the highest metal concentrations, which is likely a reflection of the abundance of zinc sources seen in the table above, as well as the metal-using industries present in the catchment. Most industrial areas have either colour steel or painted/ unpainted galvanised roofing, which are major contributors of elevated zinc during rainfall to a catchment (Charters et al., 2017; Charters et al., 2016; Kennedy and Sutherland, 2008).

Although the exact presence or percentage of painted/ unpainted galvanised roofs in the Haytons Stream catchment was not quantified in this study, there is a clear abundance of old, industrial buildings that

are likely high sources of zinc to Haytons Stream. As the stream emerges directly from the stormwater network that drains this dense industrial land, all highly metal-contaminated runoff from aged building roofs/ sidings is transferred directly and untreated into the waterway at Waterloo Road. It is probable that the metals found in this study throughout Haytons Stream sediment are the result of years of continual legacy contamination from metal-laden industrial runoff in the catchment. It is unclear whether this includes the intentional point-source discharge of highly metal-contaminated waste to Haytons Stream.

The elevated nature of other metals (Cd) in this catchment alone compared to other Christchurch areas suggest that the industries present solely or in abundance within the Haytons catchment may be a point-source, for example phosphate fertiliser production, electroplating/ galvanising industries and disposal of motor oils and lubricants (Förstner, 1984; Sutherland, 2000).

Remediation

Given the elevated concentrations of a number of metals throughout the stream bed, remediation of sediment may be a preferable if not essential task to undertake in order to improve the long-term water quality of Haytons Stream, and to reduce the impact the stream has on the water quality of the Heathcote River/ Ōpāwaho. Remediation can typically include the following; natural recovery, enhanced natural recovery, capping, in-situ treatment or dredging/ disposal (Chapman et al., 1998). The first three are often the options of choice, as they are lowest cost and do not disturb the contaminated material. However, they also assume that sources of contamination have been stopped, which may never be the case for a waterway draining dense industrial land such as Haytons Stream.

Reduction and treatment of metal-contaminated stormwater from entering the Haytons Stream catchment may be first priority, to ensure that any remediation would not succumb to the same fate of existing Haytons Stream bed sediment through time. This exact point appears to have manifested along the re-aligned section of Haytons Stream (constructed in 2012), where 150 mm of river gravels were originally placed as new stream substrate (Jerry Schutte, personal communication, September 2017). The thick silts that have since deposited now hold ecologically dangerous concentrations of metals (deposited in this area in under five years), and highlight the need to mitigate metal pollution at source, as well as through potential sediment remediation techniques.

It can be difficult to attach desired restoration outcomes or judge the success of remediation in an industrial urban stream. Working within ANZECC (2000) recommendations, it may be necessary to have a desired target ecosystem condition, as well as an appropriate control location to determine the success of any remedial works. Local decision makers will need to consider their desired ecological outcomes for the future of the Haytons Stream catchment, incorporating these visions into the adoption of any remedial works.

2.5 Conclusions

A one-off sediment survey and re-characterisation was conducted throughout Haytons Stream, using a pseudo-total digest and a weak acid (1M HCl) extraction to represent labile or 'bioavailable' trace element concentrations. From both these analyses, the Haytons Stream bed sediment was found to contain elevated concentrations of trace elements beyond that of other Christchurch catchments, as well as elevated TP (particularly in the middle catchment). Zn and Cd were the metals of highest concern (concentration relative to guidelines) and mobility (bioavailable concentrations) throughout Haytons Stream, representing significant contaminants in the upper and middle sections of the catchment. These concentrations were unexpectedly high, especially when considering the significant increase in concentrations since the last major sediment survey in 2009, and the realignment of the lower section of Haytons Stream approximately five years ago. A number of trace element concentrations (Zn, Cu, Pb, and Ni) had strong correlations with each other, suggesting they all increase in concentration together, and are potentially from a similar source, such as industrially-derived road dust and runoff.

These metals have likely the result of years of continual industrial legacy pollution, which continue to impact the stream's health today. HCl-extracted metal concentrations were similar to a number of pseudo-total metal concentrations, suggesting that metals are bioavailable to any organisms present and readily re-released to the water column throughout the bed sediment of Haytons Stream. Remediation may therefore be necessary to improve the ecological condition and water quality throughout the stream, given these implications from the trace elements found in the sediment.

Chapter 3 Baseflow, stormflow and reactive sampling of contaminants in Haytons Stream

3.1 Introduction

In urbanised landscapes, the 'urban stream syndrome' of degraded stormwater and receiving water quality is a common condition from high impervious surface coverage and increased contaminant generation in urban areas. Haytons Stream in Christchurch, New Zealand is a classic exemplar of a waterway suffering from the 'urban stream syndrome', being a tributary of the Heathcote River/ Ōpāwaho that begins its open-channel flow draining the stormwater network of a highly industrialised catchment. As a result, Haytons Stream has elevated concentrations of water and sediment contaminants when compared to other waterways in the Heathcote River catchment and across Christchurch (Margetts and Marshall, 2016; Pattle Delamore Partners, 2007). These contaminants not only result in the severely depleted aquatic biodiversity seen throughout Haytons Stream (McMurtie, 2002), but also in the downstream pollution of the Heathcote River/ Ōpāwaho and significantly higher concentrations of contaminants in the Heathcote River downstream of the Haytons Stream confluence (Pattle Delamore Partners, 2007). The previous chapter has outlined and verified the poor quality of the bed sediment throughout Haytons Stream, with elevated concentrations of trace elements throughout the catchment.

The aims of this chapter were to conduct baseflow (dry weather) and stormflow (wet weather) sampling to further quantify the contaminants present throughout Haytons Stream, and observe how their presence or concentration changes both spatially and temporally (with weather events). Spatial and temporal contaminant concentrations in the stream may give indications to specific sources of the sampled contaminants, as well as the mechanisms by which contaminants are transported from within the catchment to the waterway itself. Additionally, reactive sampling (instream or of visible pipe discharges) was undertaken when a pollution event/ discharge was observed in the catchment, to increase the understanding of which (and how) contaminants are being inappropriately discharged to Haytons Stream during dry weather.

3.2 Methods

3.2.1 *Sampling site selection*

Sampling sites were selected in consultation with Environment Canterbury. Sites were chosen based on historical data collection and new areas of interest (Figure 2.1). The ten sampling sites described in chapter two for sediment were sampled for total and dissolved trace elements, with three sites also sampled for TSS, nutrients and *E. coli* (Waterloo Road, Washbournes Road and upstream of the Wigram Retention Basin).

3.2.2 *Physio-chemical data collection*

A HACH 40d field meter was used to measure pH, temperature, conductivity and dissolved oxygen (DO) in-situ at each site. The pH values at the three additional contaminant sites were used to calculate 95% species protection ammoniacal-nitrogen trigger values, which are pH dependant.

3.2.3 *Sample strategy, collection and analysis*

Rainfall

Rainfall data was taken from NIWA's rainfall station at Kyle St (5.4 km from Waterloo Road) in Christchurch (-43.53074, 172.60769), which was accessed via NIWAs online National Climate Database, 'CliFlo'. Baseflow and stormflow sampling events were conducted with at least 2-3 antecedent dry days (ADD) ignoring <1 mm of rainfall. This was to ensure that baseflow sampling was not impacted by a previous rainfall event, and that stormflow sampling was conducted in the presence of substantial rainfall, after a similar period of dry days to allow the build-up of contaminants on impervious surfaces.

Parameter analysis

Trace element samples were collected with new pre-labelled 120 ml polypropylene (PP) containers, which were rinsed with ~20-30 ml of stream water then filled. New nitrile gloves were worn at each sampling site, to avoid potential cross-contamination. Each sample bottle was then bagged in a plastic sandwich bag to prevent cross contamination in the field or in transport, before being placed in a chilly bin on ice bricks to keep samples under 4ºC, avoiding excess particle formation from growth and aggregation of bacteria (Batley, 1989).

Samples were taken to the environmental engineering laboratory at the University of Canterbury, where 10 ml of each dissolved metal sample was immediately filtered through a 0.45 µm filter, straight into pre-labelled ICP-MS tubes. Dissolved samples were then preserved with a few drops of 70% trace grade nitric acid to reduce the pH <2. Total metal samples were analysed with a nitric acid digestion following

analytical method APHA 3125B (Table 3.1 outlines all analytical methods for all sampled parameters). 25 ml of sample (via pipette) and 5ml of 70% trace analysis grade nitric acid were added to 50 ml centrifuge tubes and boiled in a digestion block for 1 hour and 15 mins, before cooling. 10 ml of each sample was then filtered through a 0.45µm disposable filter into ICP-MS tubes. Laboratory blanks (using de-ionised water), duplicates and triplicates were included in every analysis run for quality control to provide a check for clean and consistent lab work. Due to initial data identifying ICP-MS detection limit and interference issues, it was deemed that the samples had excessive levels of salts and metals, and were subsequently diluted 10 times (0.5 ml sample with 4.5 ml 2% nitric acid) before each analysis, prepared in a metal-free clean room. Samples were analysed for trace elements via ICP-MS as in Chapter Two section 2.2.3.

Total Suspended Solid samples were collected using 1 litre polypropylene jars, and stored in a chilly bin during transport back to the University of Canterbury for analysis within 24 hours in accordance with analytical method APHA 2540 D (filtering/ weighing through GFC filter and drying at 105ºC) in the environmental engineering laboratory at the University of Canterbury.

Nutrients (NH_4-N, DRP and NNN) were all collected in the same 500 ml HDPE bottle, obtained from Hill Laboratories in Hornby, Christchurch. Bottles were pre-rinsed with sample water before filling, labelling and storage in a chilly bin.

E. coli samples were collected in a sterilised plastic jar collected from Hill Laboratories, where a sample was directly taken from the stream without prior rinsing. Both *E. coli* and nutrient samples were taken to Hill Laboratories within a few hours of sampling, with a completed chain of custody form (COC-example provided in Appendix 3) outlining the tests required, in line with pre-determined quotes.

A hydrocarbon sample was taken if an observed discharge suggested their presence (i.e. slicks or odours present). Hill Laboratories' brown organic glass 500 ml bottles were used to collect sample water (with sulphuric acid preservative for TPHs), which were stored in a chilly bin until transport to the analytical lab's site on Waterloo Road.

Table 3.1- Analytical methods for all sampled parameters

Parameter		Acronym	Units	Analytical method	Description
Trace elements		tm/dm	µg/L	APHA 3125B/3030E (for total)	Boiling nitric acid/ICP-MS analysis
Sediments	Total Suspended Solids	TSS	mg/L	APHA 2540 D	Filtration, gravimetric
Nutrients	Ammoniacal-Nitrogen	NH_4-N	mg/L	APHA 4500-NH_3 F	Phenol/hypochlorite colorimetry
	Dissolved Reactive Phosphorous	DRP	mg/L	APHA 4500-P E	Molybdenum blue colorimetry
	Nitrate-Nitrite Nitrogen	NNN	mg/L	APHA 4500-NO_3^- I	Automated cadmium reduction, flow injection analyser
Microorganisms	*Escherichia coli*	*E. coli*	MPN/100 ml	APHA 9223 B	MPN count using Colilert
Hydrocarbons	Polycyclic Aromatic Hydrocarbons	PAHs	mg or µg/L	US EPA CLP Method (modified)	GC-MS SIM analysis
	Total Petroleum Hydrocarbons in Water	TPHs	mg/L	USEPA 8015B	Solvent Hexane extraction, GC-FID analysis, Headspace GC-MS FS analysis

3.2.4 *Quality Assurance/ Quality Control*

Blanks and duplicates (field and laboratory method) were included in every sampling run for QA/QC, and were predominantly below 10% difference. As this study dealt with a large range and variation of concentrations (low to highly elevated), some duplicates had over 10% difference. Appendix 4 provides averages of the percentage difference between original samples and duplicates for all sampling runs for total and dissolved metals. ICP-MS internal standard reference material 1643f was used to check instrument performance for analysed elements (Table 3.2).

3.2.5 *Data analysis*

Statistical analysis was carried out on all sampled parameters, to compare means and analyse for significant differences between weather events and sampling sites, in Microsoft Excel. Due to the statistically small sample sizes for weather events (n=3), data was log transformed to assume normality at the low n value, which therefore took the geometric (and not arithmetic) mean. A t-test was then adopted for all contaminants sampled during baseflow and stormflow. Differences in contaminant means were considered significant at p-value ≤ 0.05.

Table 3.2 QA/QC data for water metal sampling

Baseflow 1, 2 & Stormflow 1				Stormflow 2,3 & Baseflow 3		
Element	Detection Limits (µg/L)	Average blanks (tot/diss µg/L)	CRM 1643f Recovery %	Detection Limits (µg/L)	Average blanks (tot/diss µg/L)	CRM 1643f Recovery %
Mg	0.1	6.48 /7.98	110	1	4.28 /1.66	96
Al	1	51.9 /6.49	103	1	40.7 /5.07	98
Ca	10	210 /950	102	1000	<DL	95
Ti	1	<DL	-	1	2.04 /1.82	-
V	0.1	<DL	101	0.1	<DL	97
Cr	0.1	0.63 /<DL	103	1	0.2 /<DL	96
Mn	0.1	0.2 /0.11	106	0.1	<DL	86
Fe	1	7.03 /<DL	109	1	4.52 /<DL	96
Co	1	1.39 /1.07	94	0.1	0.13 /<DL	90
Ni	0.1	0.21 /<DL	102	1	2.93 /<DL	93
Cu	0.1	2.37 /0.77	95	0.1	2 /11.4	89
Zn	0.1	7.69 /2.61	104	1	<DL /5.8	83
As	0.1	0.11 /<DL	107	0.1	<DL	102
Cd	0.1	0.23 /<DL	105	1	<DL	99
Sb	0.1	0.92 /0.37	110	0.1	0.84 /0.71	107
Pb	0.1	0.25 /0.11	102	0.1	0.15 /0.35	95

Hardness modified trigger values

During every sampling event, instream calcium and magnesium content was averaged across the eight sites along Haytons Stream (as sites held similar Mg and Ca concentrations) to gain a rough understanding of instream conditions for the given event. Depending on how 'hard' water is, recommended metal guideline values can change accordingly (i.e. higher guideline concentrations with harder water). Calculations from Table 3.4.3 of the ANZECC guidelines (hardness-dependant algorithms) were adopted when water hardness was greater than soft, calculated for each metal with a guideline. This was adopted to ensure that the most applicable metal guidelines for aquatic organisms were used throughout Haytons Stream. The algorithms used are outlined in Appendix 4.

3.3 Results

3.3.1 *Meteorological data*

Rainfall data during all sampling events are presented in Table 3.3, with Figure 3.1 showing the total rainfall over the entire research sampling period (red arrows representing baseflow events, green arrows representing stormflow events).

Table 3.3 Meteorological data for water sampling campaigns

Event	Date	Antecedent Dry Days (ADD)	Total Rain Depth	Rainfall Duration (hours)
Baseflow 1	23/5/17	3	-	-
Baseflow 2	29/5/17	2	-	-
Stormflow 1	21/7/17	3	31.8	12
Baseflow 3	18/8/17	3	-	-
Stormflow 2	1/9/17	12	8	14
Stormflow 3	7/10/17	14	15.2	40

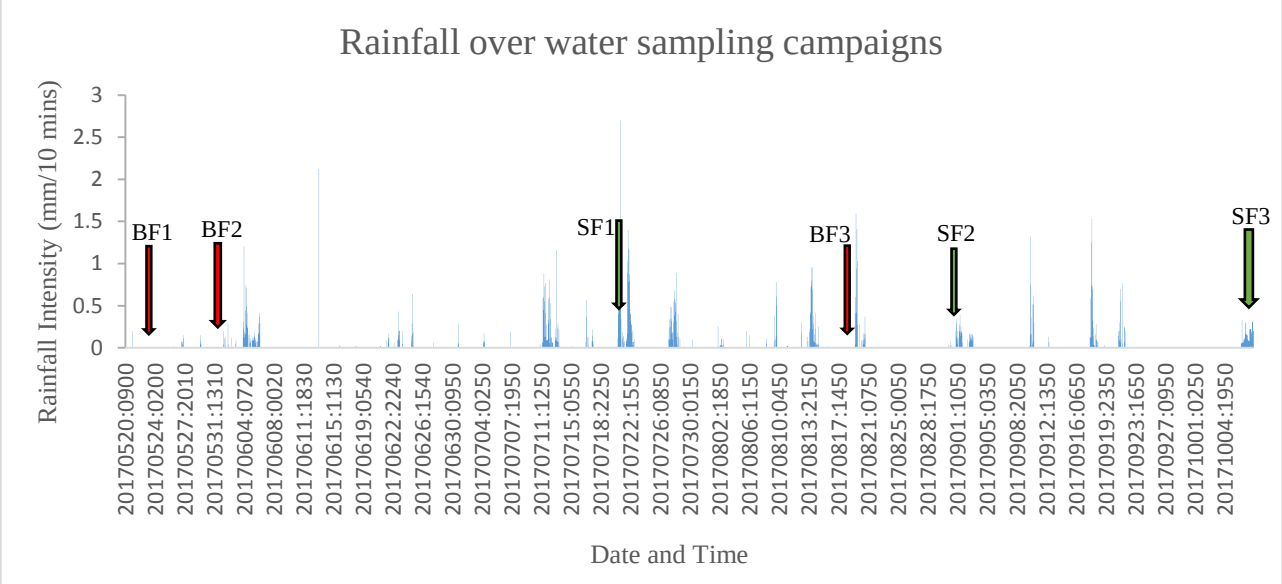


Figure 3.1 Rainfall over all sampling events

The three stormflow sampling events, and the period of time over which samples were collected relative to rainfall is displayed in Figure 3.2. Sufficient time (at least three-four hours) of rainfall at around 0.5-1mm/ hour intensity was allowed to fall before samples were collected from the stream. This delay was to allow stormwater to pass through piped infrastructure, into the stream, and to follow previous

protocol adopted by Moores et al. (2009), compensating for the attenuating effect the Wigram Retention Basin has on the discharge of water from Haytons Stream to the Heathcote River.

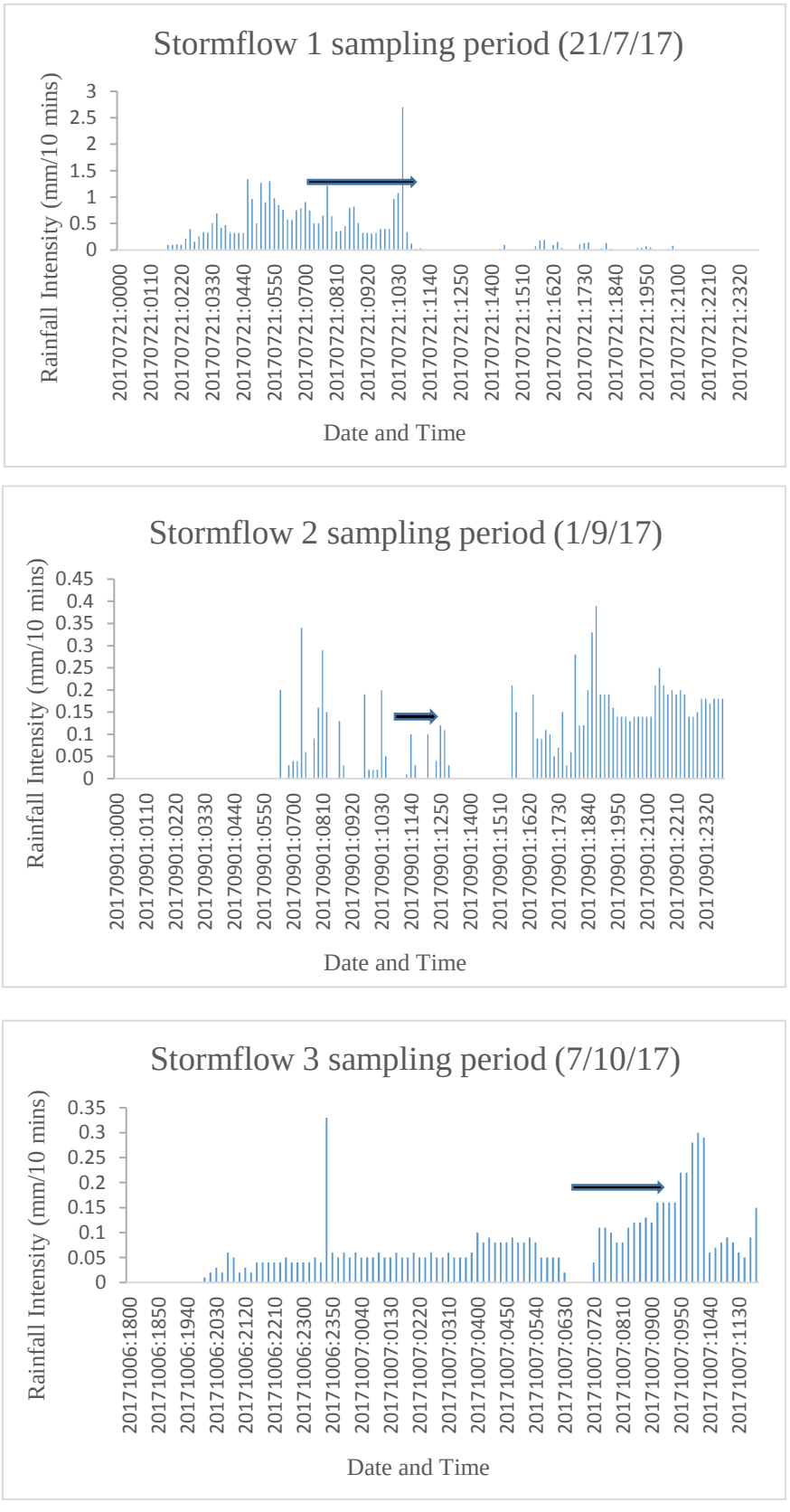


Figure 3.2 Sampling times over each storm event

3.3.2 *Water quality data*

3.3.2.1 Physio-chemical data

The physio-chemical data from all six sampling campaigns, with means (in bold) and range (pH has median reported) is presented in Table 3.4. Each parameter is then discussed individually below.

Table 3.4 Physio-chemical data across Haytons Stream

Baseflow					
Site	Temperature (ºC)	pH	Conductivity (µS/cm)	Dissolved Oxygen (mg/L)	DO % Saturation
WAR	**11.7** (10.9 - 3.1)	**7.41** (7.22- 7.41)	**125** (111-151)	**8.06** (4.37-10)	**76** (40.2 -94.9)
GCP	**9.5** (8.8 –10.1)	**7.29** (6.62- 7.35)	**143** (138-153)	**5.72** (2.85-8.24)	**50.4** (25.6 -72.7)
WBR	**10.8** (10 -11.6)	**7.37** (6.96- 7.39)	**134** (117-145)	**8.37** (7.73-8.98)	**76.3** (70.6 -81.4)
LSA	**9.4** (7.8 -10.8)	**7.35** (6.8- 7.59)	**95.1** (77.3-122)	**8.81** (6.45-10.2)	**77.9** (56.1 -90.1)
TRW	**8.8** (7.3 -9.5)	**7.07** (6.54- 7.38)	**107** (75.2-155)	**7.1** (4.83-8.31)	**61.6** (42 -72.5)
WGR	**9.8** (8.3 -10.7)	**7.38** (6.94- 7.53)	**130** (104-175)	**10.3** (8.99-11.3)	**92** (80.4 -103)
UWB	**12** (9.8 -13.5)	**7.07** (6.53- 7.26)	**180** (168-200)	**7.82** (6.31-9.02)	**73.6** (56.5 -103)
DWB	**9.4** (7.5 -11)	**7.35** (6.53- 7.73)	**112** (86.4-139)	**10.6** (9.74-11.4)	**93.9** (90.3 -99.8)
HEA-UHS	**12.5** (12 -13.4)	**6.79** (6.19- 6.9)	**324** (306-334)	**6.33** (4.33-8.12)	**60.2** (40.4 -79.6)
HEA-DHS	**11** (9.6 -12.7)	**6.97** (6.28- 7.2)	**211** (209-212)	**9.23** (8.44-10)	**85.1** (76.6- 89.7)
Stormflow					
WAR	**11.5** (9.6 -13.8)	**7.37** (7.35 -8.57)	**88** (30- 164)	**9.46** (8.84 -10.5)	**88** (81.8 -96.7)
GCP	**10.6** (9.2 -12.5)	**7.49** (7.07 -8.54)	**97** (28.9 -188)	**9.04** (8.07 -10.5)	**82.4** (71.9 -95.1)
WBR	**10.4** (9.5 -12.2)	**7.22** (7.01 -7.25)	**160** (40.5 -291)	**9.75** (9.09 -10.6)	**88.3** (84.3 -96)
LSA	**10.2** (9.3 -11.9)	**6.95** (6.91 -6.97)	**124** (28.8 -214)	**9.64** (8.81 -10.3)	**87** (81.6 -93.3)
TRW	**10.1** (9.2 -11.8)	**7.01** (6.67 -7.14)	**143** (28.1 -252)	**7.93** (7.60 -10.1)	**71.3** (56.5 -91.3)
WGR	**10** (8.9 -11.6)	**6.74** (6.58 -7.13)	**151** (31.9 -297)	**9.15** (6.80 -10.8)	**82** (62.5 -94.4)
UWB	**10.2** (9 -11.7)	**6.87** (6.42 -7.33)	**138** (34.4 -197)	**9.45** (7.53 -11.6)	**85** (69.3 -102.5)
DWB	**10.5** (9 -12.8)	**6.96** (6.85 -7.59)	**125** (99.7 -156)	**10.2** (8.70 -11.7)	**92.6** (82 -103)
HEA-UHS	**11.8** (10.8 -12.5)	**6.71** (6.59 -6.84)	**296** (252 -322)	**6.09** (3.12 -8.67)	**57.2** (29.2 -81.1)
HEA-DHS	**11.1** (9 -12.5)	**6.62** (6.49 -6.66)	**238** (120- 298)	**7.61** (3.34 -9.90)	**70** (31.3 -91.9)

Conductivity

During baseflow the highest conductivity in Haytons Stream was consistently at UWB (180 µS/cm average). The lowest average dry weather conductivity was at LSA (95.1 µS/cm), after the confluence with Paparua Stream. HEA-UHS constantly had the highest recorded conductivity during sampling, with a mean of 324 µS/cm in dry weather and 296 µS/cm in wet weather. The highest average stormflow conductivity in Haytons Stream was at WBR (160 µS/cm). Haytons Stream appeared to consistently dilute the Heathcote River's conductivity, with a lower value recorded after the confluence during every sampling run. There were no significant differences between baseflow and stormflow conductivity throughout Haytons Stream, or for any other physio-chemical parameters. DWB had significantly lower baseflow conductivity than UWB (p =0.04), as did HEA-DHS compared to HEA-UHS (p =0.004).

Dissolved Oxygen

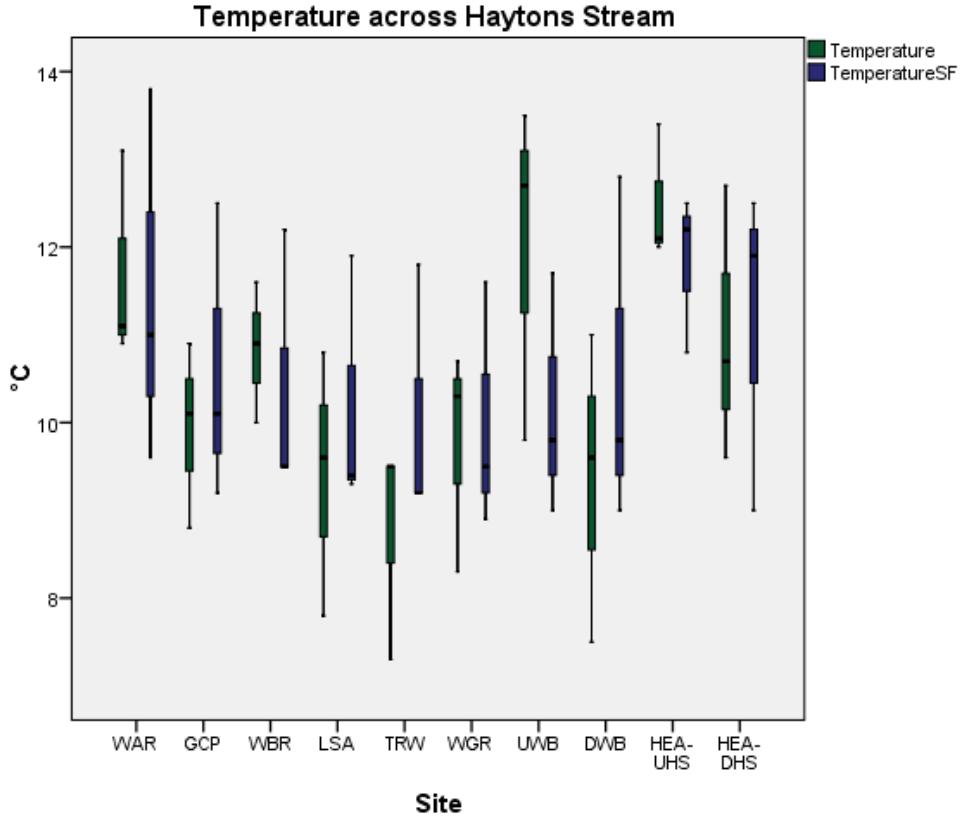
The concentration of dissolved oxygen varied throughout Haytons Stream, especially during dry weather. Baseflow DO was lowest at GCP on average, with a mean of 5.72 mg/L. However it should be noted that a DO concentration of 2.85 mg/L skews this, compared to the other concentrations of 6.07 and 8.24 mg/L at GCP. The highest DO during baseflow was consistently at DWB, with a mean of 10.6 mg/L. Baseflow DO was consistently below the Environment Canterbury urban stream guideline of ≥80% saturation at all times, throughout the length of Haytons Stream. Stormflow DO concentrations were higher and more consistent, with the lowest average concentration at HEA-UHS (6.09 mg/L) and the highest at DWB (10.2 mg/L). The lowest average stormflow DO on Haytons Stream was at TRW (7.93 mg/L).

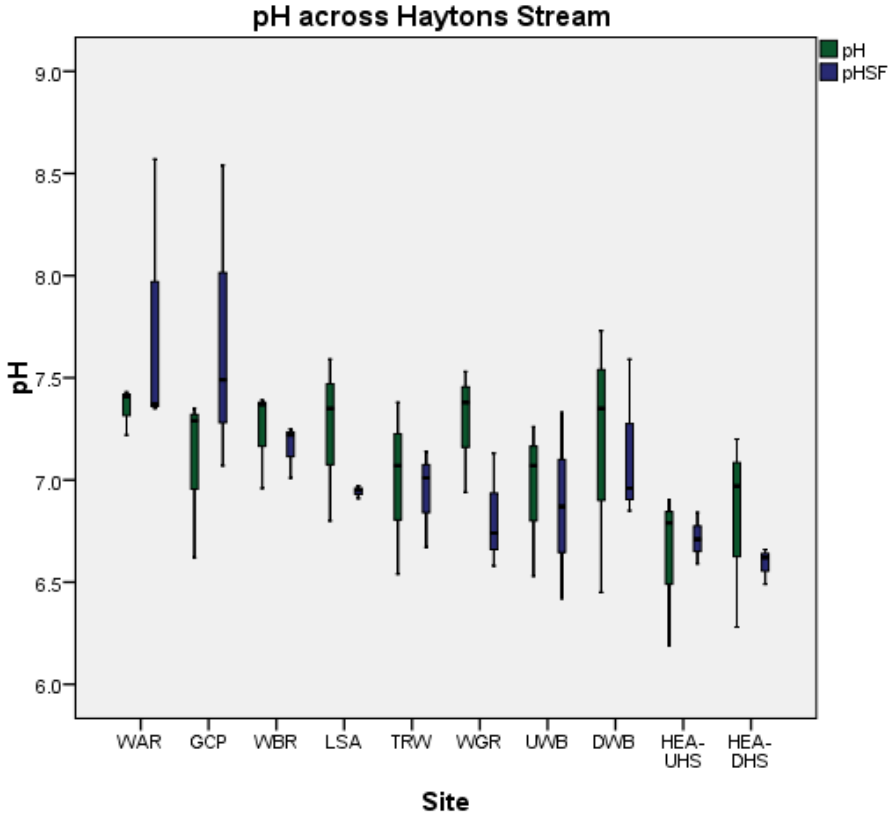
pH

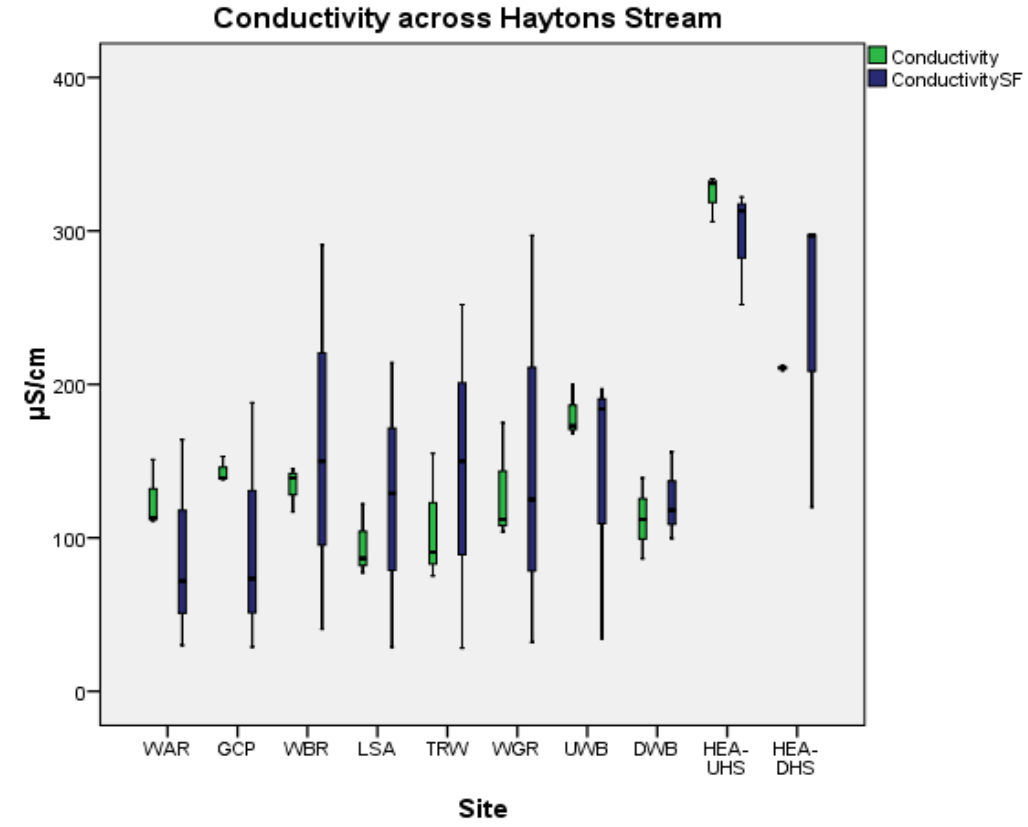
The pH was consistent during baseflow throughout Haytons Stream, with no drastic changes between sites. The highest median pH in baseflow was at Waterloo Road, at 7.41. The Heathcote River upstream of the confluence consistently had the lowest pH during baseflow conditions (median 6.79 compared to a median of 7.35 for all Haytons Stream), and was consistently higher downstream of the confluence (median pH 6.97 at HEA-DHS) compared to upstream. In stormflow, median pH was highest at GCP (7.49) and lowest at WGR (6.74). The single highest pH of 8.57 was recorded at WAR during stormflow one.

Temperature

Instream water temperature varied little between dry and wet weather sampling in Haytons Stream, with most sites on average having slightly higher temperatures during stormflow. During baseflow, temperature ranged from 7.3- 13.5ºC in Haytons Stream, and from 8.9- 13.8 ˚C in stormflow. Highest temperatures in dry weather were consistently found at Waterloo Road (WAR) and upstream of the Wigram Retention Basin (UWB) in dry weather, whereas temperatures were consistently uniform in wet weather and varied by a maximum of 1.8 ˚C across all sites (Figure 3.3).


Temperature across Haytons Stream
Temperature
TemperatureSF
°C
14
12
10
8
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site


pH across Haytons Stream
pH
pHSF
pH
9.0
8.5
8.0
7.5
7.0
6.5
6.0
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site



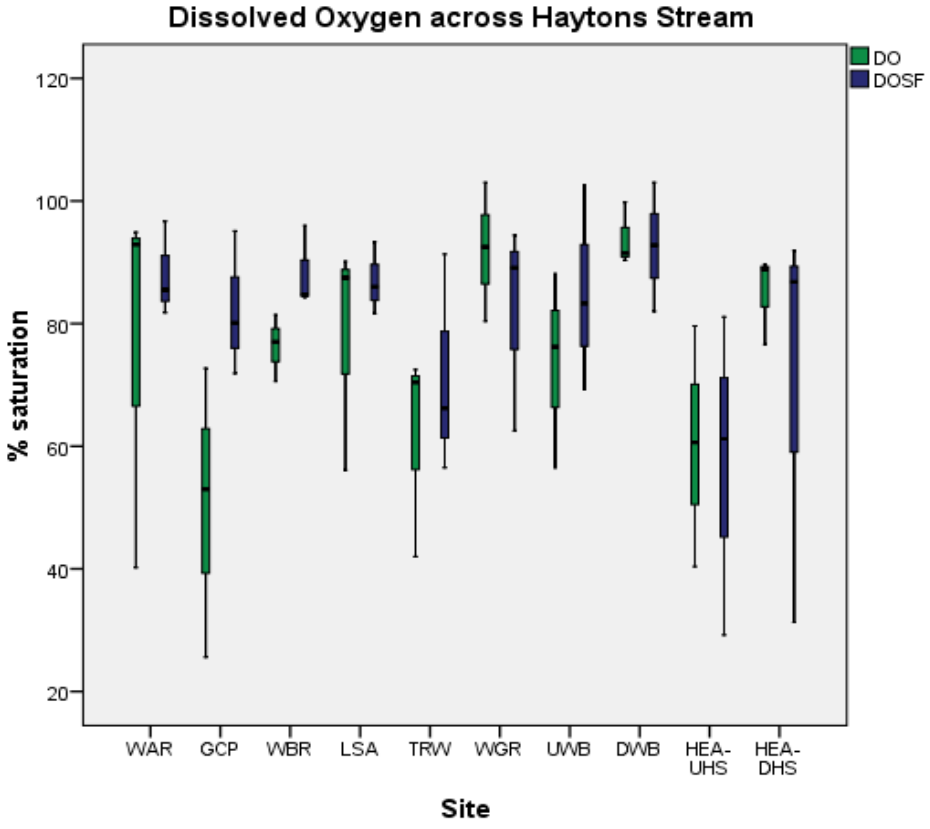
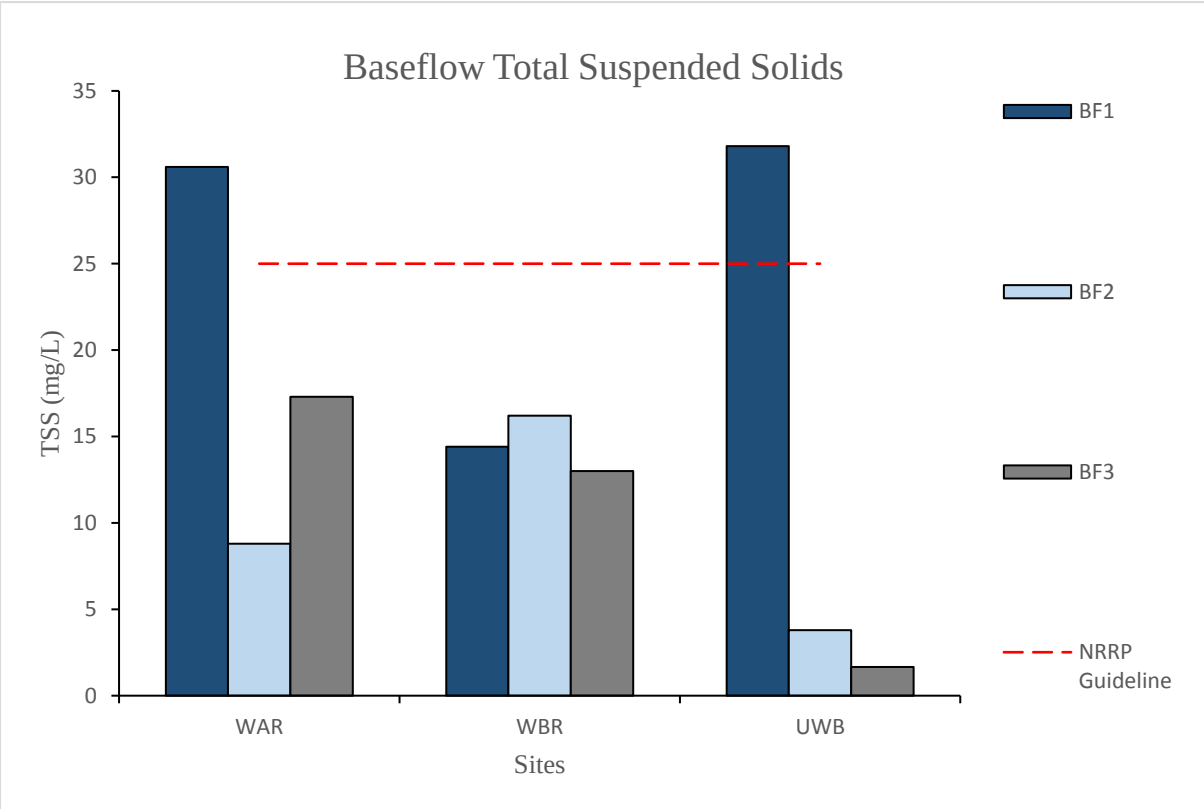


Figure 3.3 Baseflow (green) and stormflow (SF) physio-chemical data across Haytons Stream

3.3.2.2 Total Suspended Solids

TSS was sampled at the three intensive sampling sites of Waterloo Road, Washbournes Road and Upstream of the Wigram Retention Basin. TSS concentrations were compared to the Canterbury Natural Resources Regional Plan (NRRP; now Land and Water Regional Plan (LWRP) guideline of 25 mg/L (Figure 3.4). In dry weather, TSS was highest on average at WAR (18.9 mg/L average) and lowest at UWB (12.4 mg/L average). UWB had the single highest (30.6 mg/L) and lowest (1.67 mg/L) concentrations of TSS during dry weather, which may be explained due to construction and maintenance activities (which generate dust particulates) occurring in this area throughout the sampling campaign. There were no statistically significant differences in TSS during baseflow between any sites.

During stormflow, TSS was typically much higher, with a peak concentration of 779 mg/L at WAR, coinciding with an excessive level of pollen in the stream and exiting the Waterloo Road stormwater network. Again, WAR consistently had the highest concentrations of stormflow TSS, with UWB recording the lowest value of 0.66 mg/L during SF2. Average concentrations at WAR, WBR and UWB were 315, 44 and 25.8 mg/L respectively. It should be noted that the stormflow two TSS concentration of 779 mg/L significantly skews the WAR average upwards, with the median stormflow TSS concentration being 150 mg/L at this site. Consistent with baseflow, there were no statistically significant differences in TSS between sampling sites during stormflows. There were also no significant differences in TSS between baseflow and stormflow between individual sites and throughout all of Haytons Stream.



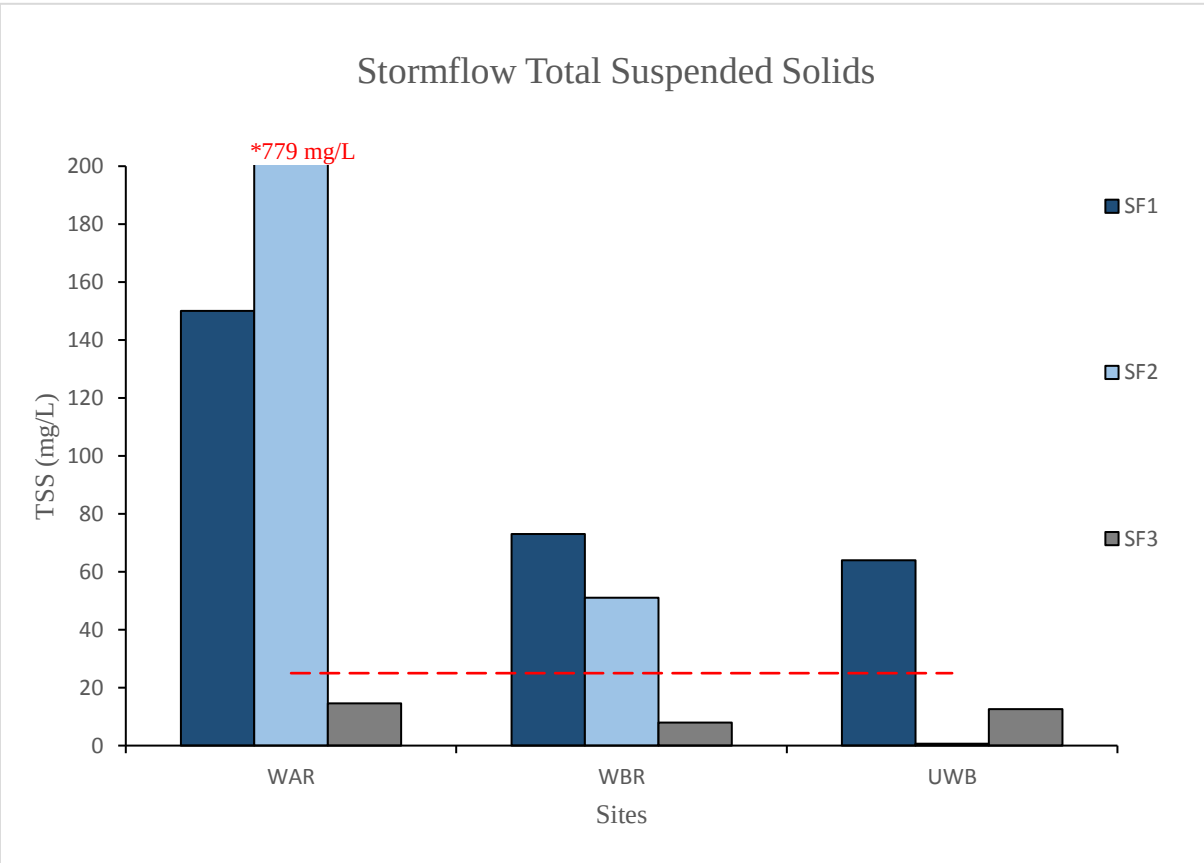


Figure 3.4 Total Suspended Solids in Haytons Stream

3.3.2.3 Trace elements

The full dataset of total and dissolved trace element concentrations at all sites, for all sampling events is provided in Appendix 4. For every sampling event (except stormflow two), water hardness was soft (range; 18.3- 52.7 mg/L $CaCo_3$), and thus normal ANZECC metal guideline values applied. During stormflow two, water hardness was 62.8 mg/L as $CaCo_3$ and thus was of 'moderate' hardness. Each individual guideline then had a re-calculation to determine the new appropriate guideline value and species protection level, which are presented in Appendix 4 for reference. Despite modifying for hardness, the metals Al, Cu and Zn consistently all still remained in exceedance of the ANZECC 80% protection guideline throughout Haytons Stream during stormflow two.

The trace elements discussed and tabled in this section are those which exceeded guidelines during one or more sampling events. Those elements are Al, As, Cd, Cr, Cu, Pb and Zn. The concentrations of total and dissolved metals described below across all sampling sites during baseflow and stormflow are presented in Figure 3.5. Many trace element concentrations were found elevated far beyond (occasionally magnitudes of difference) ANZECC species protection guidelines. Partitioning between dissolved and particulate metals was also calculated to determine what proportion of the metal concentration was in dissolved form at each sampling site (Figure 3.6).

Aluminium

Aluminium was frequently far in exceedance of the 150 µg/L 80% guideline. Maximum total Al was 1949 µg/L during baseflow at WAR, and 8743 µg/L during stormflow (at WAR). Dissolved Al was highest at 106 µg/L at WBR during baseflow and 68.9 µg/L during stormflow at LSA. All of these sites are within industrial land in the catchment. Aluminium was predominantly present in particulate form, with most sites having around 90% particulate Al across Haytons Stream during both baseflow and stormflow. Stormflow conditions did not appear to increase or decrease the amount of particulate or dissolved Al substantially.

Arsenic

Arsenic exceeded the ANZECC 99% guideline at maximum concentrations in Haytons Stream. During baseflow, maximum total As was 2.4 µg/L at WBR and dissolved As 1.9 µg/l at DWB. During stormflow maximum total As was 5.3 µg/L at WAR. Arsenic was mostly dissolved in Haytons Stream, ranging from 76-94% dissolved during baseflow and 62-95% during stormflow. Wet weather brought slightly higher levels of particulate arsenic to the stream when compared to baseflow. Baseflow dissolved As was highest at UWB (93%), and at DWB (95%) during stormflow.

Cadmium

Cadmium varied substantially across the catchment, from 0.01-221 µg/L. During baseflow, Cd hit 2.3 µg/L at WBR (total Cd), whereas in stormflow maximum total Cd was 221 µg/L at WAR. Cd also reached 6.1 µg/L during stormflow at GCP and WBR respectively, significantly elevated beyond the 80% guideline of 0.8 µg/L. Cd ranged from 11-83% dissolved during baseflow and 13-92% dissolved during stormflow. As with other metals, particulate Cd increased at all sites during stormflow, except for HEA-UHS where the dissolved portion increased in wet weather. Dissolved Cd was highest (83%) in dry weather at UWB, and was 92% on average in stormflow at HEA-UHS.

Chromium

Maximum baseflow Cr was 17.7 µg/L at LSA on Haytons Stream, whereas baseflow Cr was highest at 22.7 µg/L at the Heathcote River. During stormflow, maximum Cr was 13.4 µg/L at WAR, with higher concentrations consistently within the first 4-5 sites in industrial land. Chromium was more particulate than dissolved during baseflow, with a range of 49-98% particulate across the catchment. In stormflow, particulates remained dominant with a range of 47-77%.

Copper

Total Cu reached 10.8 µg/L at WAR during baseflow, and dissolved Cu 2.9 µg/L at WBR. During stormflow, total Cu reached 33.4 µg/L at WBR and dissolved Cu reached a maximum of 9.3 µg/L at UWB, elevated beyond the 2.5 µg/l ANZECC 80% protection guideline. Baseflow Cu ranged from 30-68% dissolved, whereas in stormflow dissolved fractions ranged from 36-66%. Dissolved Cu tended to increase at all sites on average across the catchment with rainfall.

Lead

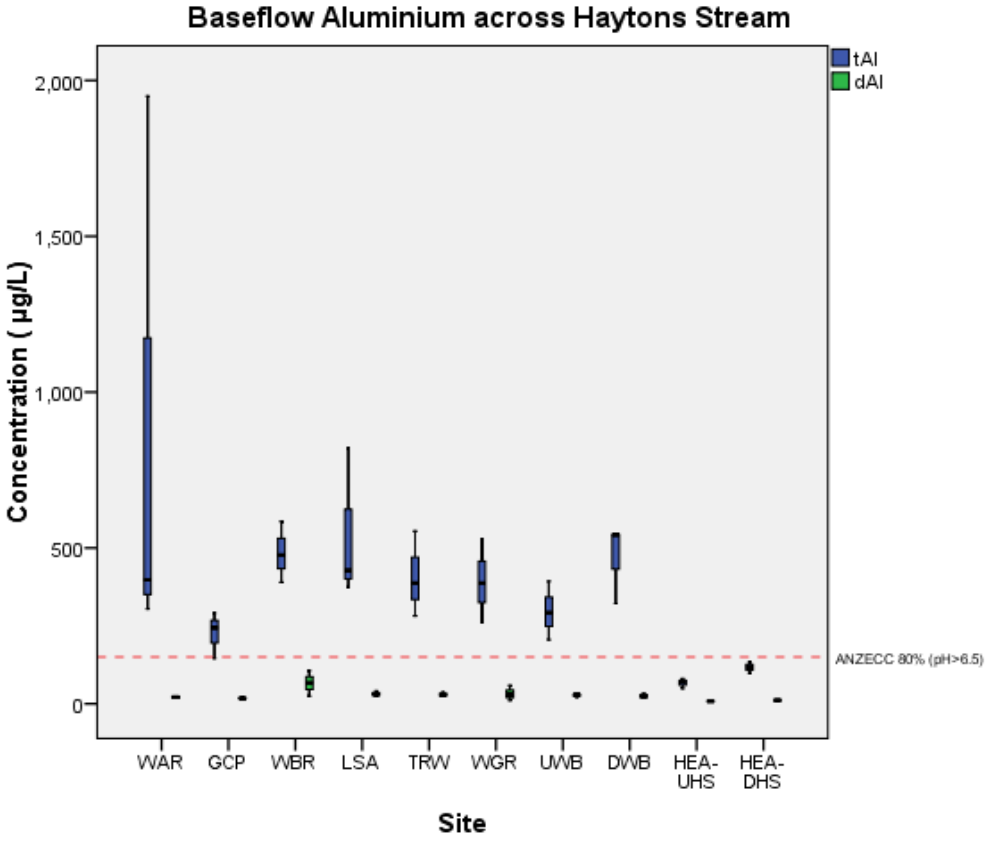
The maximum total Pb during baseflow was at Washbournes Road (11.3 µg/L), elevated beyond the 9.4 µg/L 80% guideline. Dissolved Pb during baseflow was highest at GCP, reaching 1.5 µg/L. In stormflow, maximum Pb concentrations were 31.1 µg/L for total Pb at WAR, and 1.2 µg/L dissolved Pb (also at WAR). All of these sites with maximum concentrations are located within the dense industrial land use of the catchment. Lead was predominantly particulate at all sampling sites, ranging from 14- 45% dissolved during baseflow and 7- 31% dissolved during stormflow. Rainfall brought greater quantities of particulate Pb to Haytons Stream when compared to baseflow. The highest average dissolved baseflow Pb was at HEA-UHS (45%) and highest average dissolved stormflow Pb also at HEA-UHS (31%).

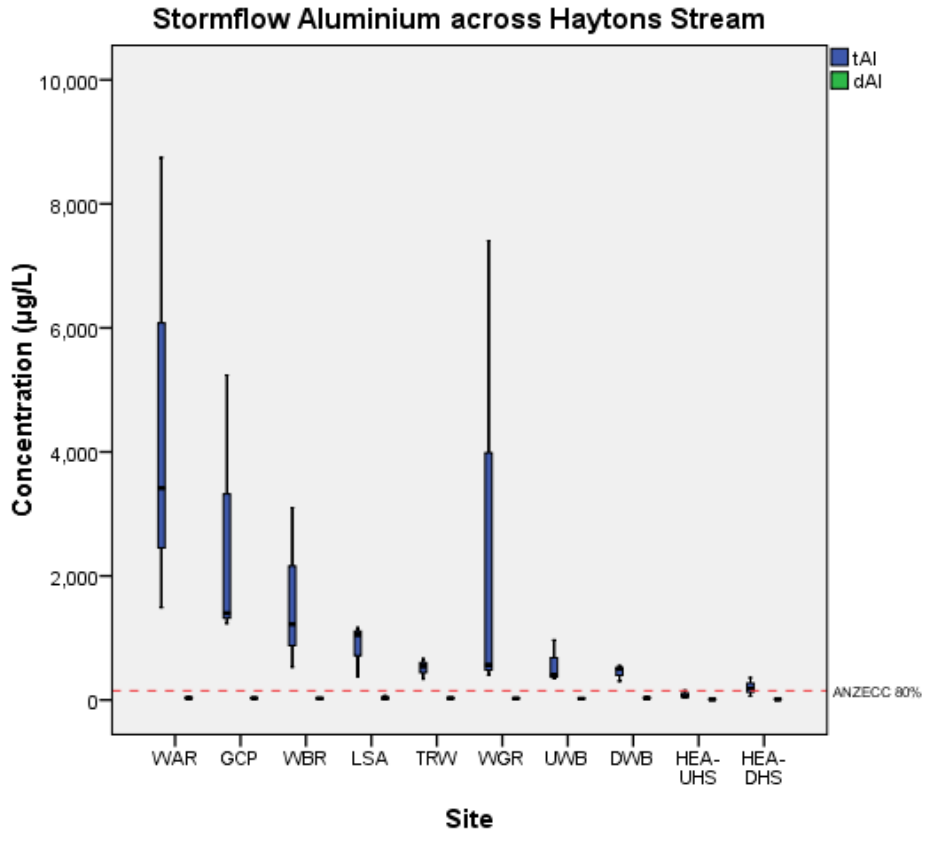
Zinc

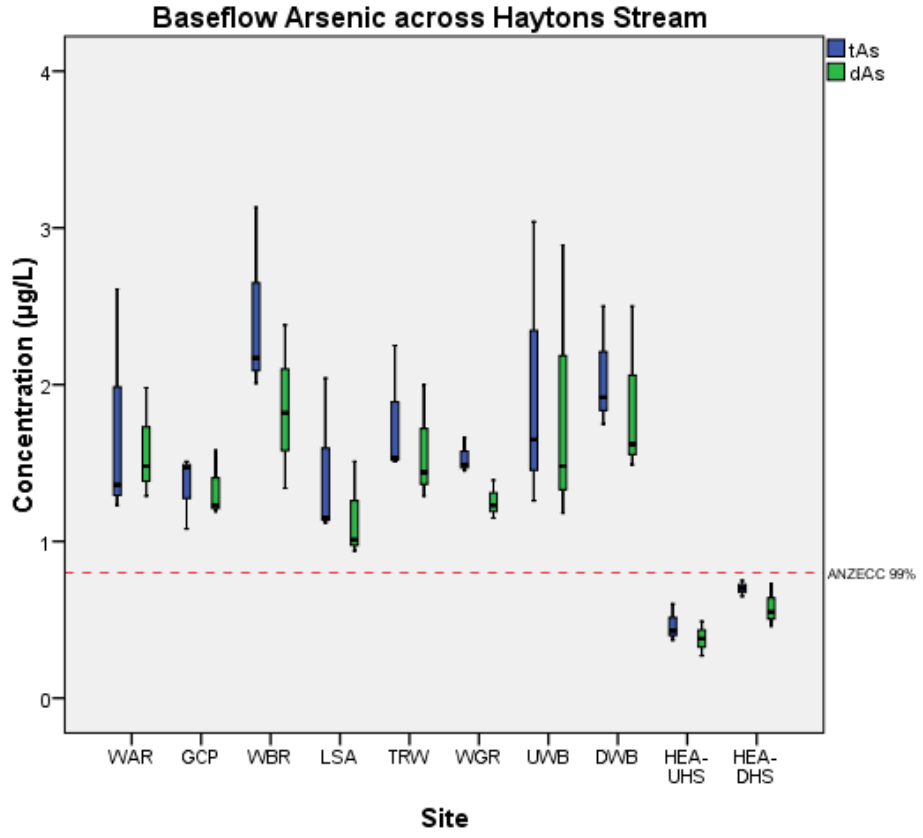
Zinc was highly elevated in the water column throughout Haytons Stream, with a maximum baseflow Zn of 1242 µg/L at Washbournes Road, representing a 40-fold exceedance of the 31 µg/L 80%

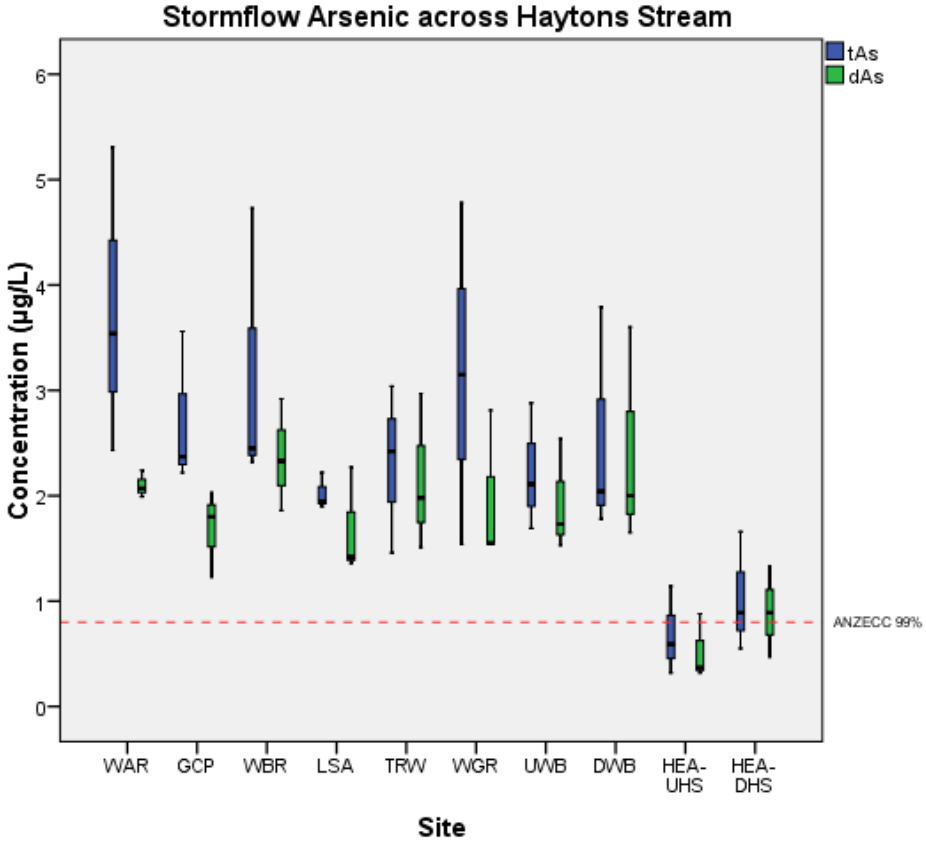
guideline. Baseflow dissolved Zn was highest at 229 µg/L, also at WBR. Maximum stormflow total and dissolved Zn were 823 and 813 µg/L (both at TRW in the lower catchment). This shows Zn was elevated throughout all weather conditions, and across the whole catchment regardless of land use. Zinc was predominantly dissolved during baseflow, ranging from 51-89% across the catchment. During stormflow particulate fractions increased, with an average dissolved range of 45-91%. The highest average dissolved baseflow Zn was at HEA-UHS at 89%, closely followed by TRW with 88%. In stormflow, highest average dissolved Zn was found at TRW, with 91%.

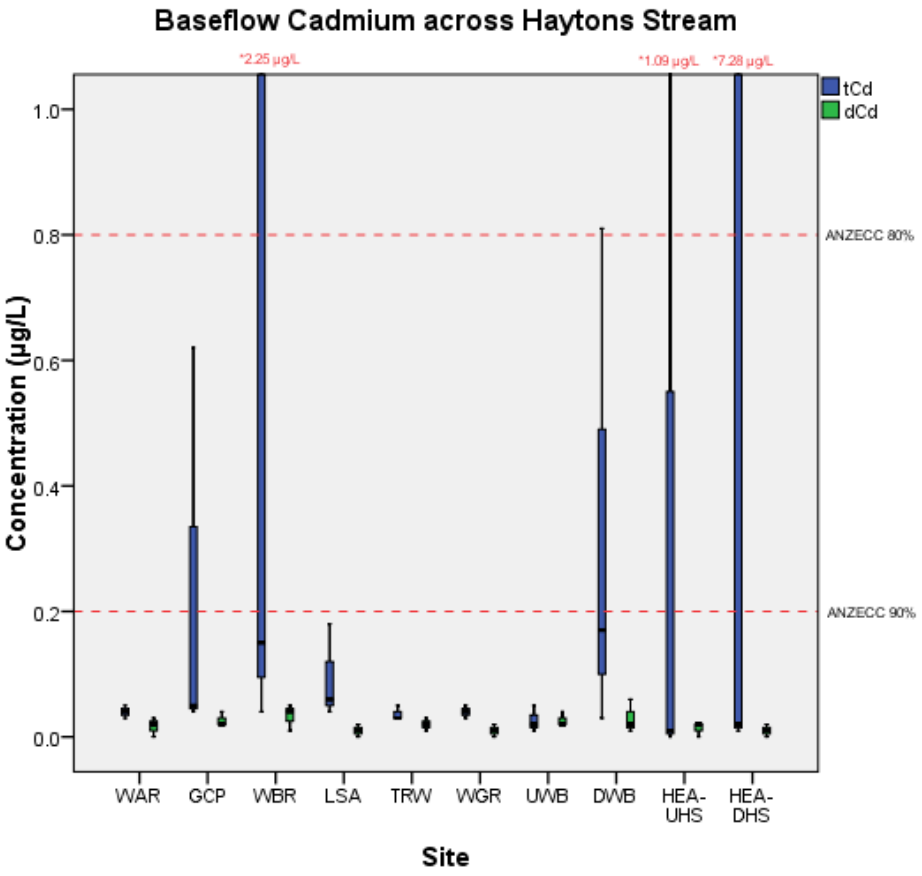
In Figure 3.5 below, large concentration spikes or maximum values have been cut out and marked with a * to denote the specific value, if they were too high and skewed other results on the graph.

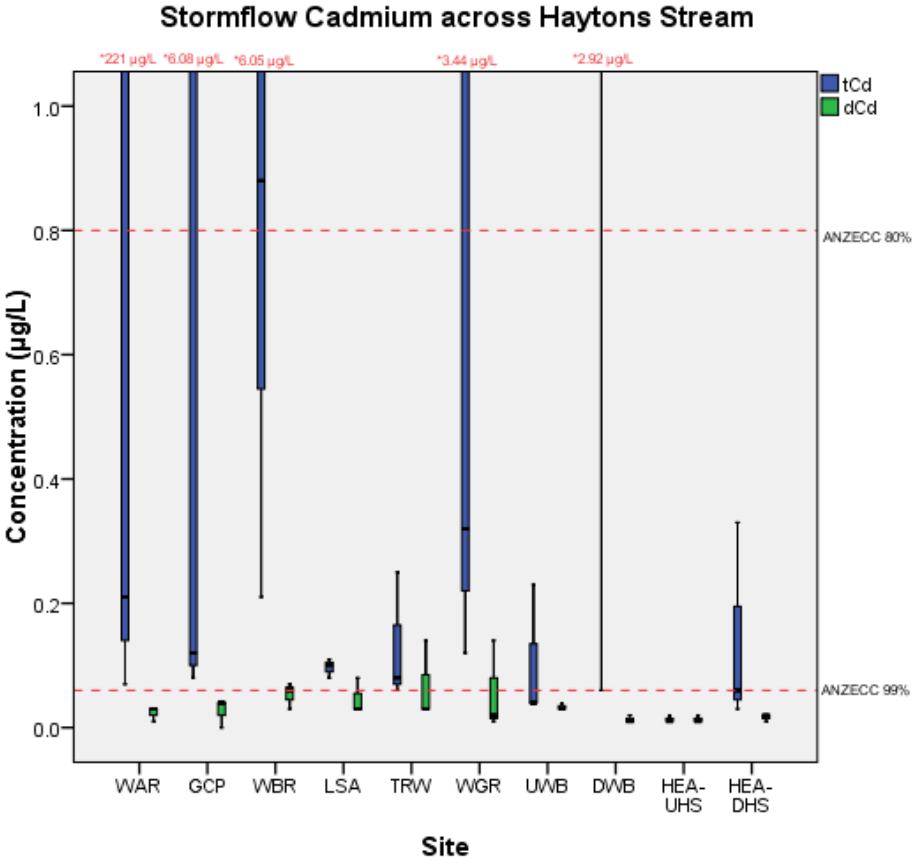

Baseflow Aluminium across Haytons Stream
tAl
dAl
2,000
1,500
1,000
500
0
Concentration (µg/L)
ANZECC 80% (pH>6.5)
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site

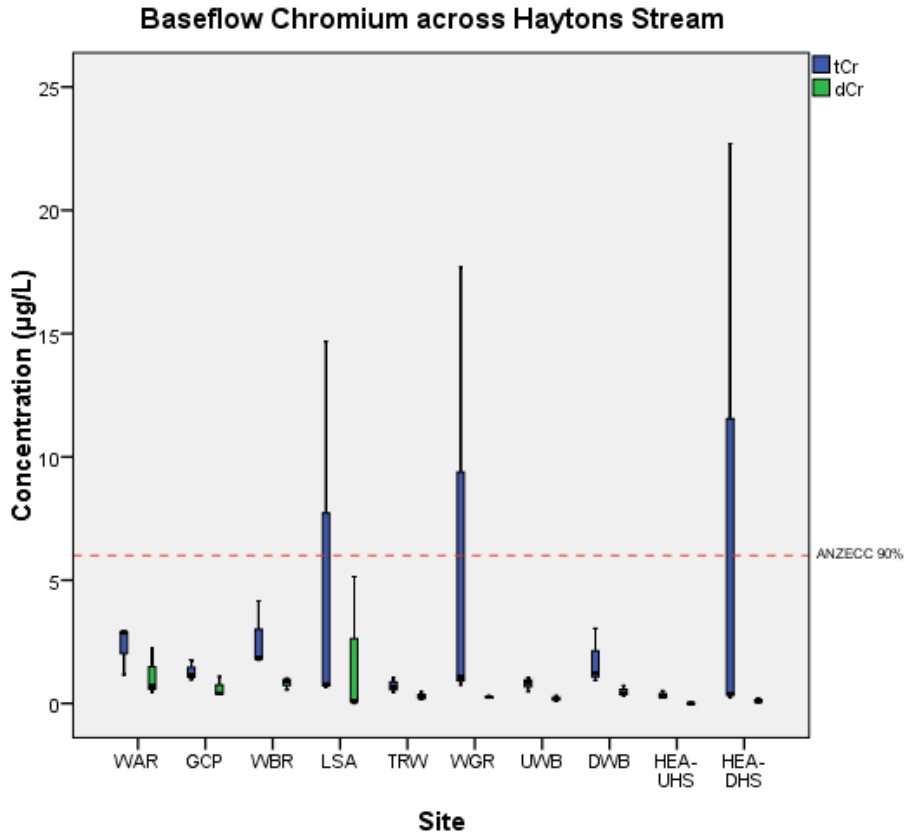

Stormflow Aluminium across Haytons Stream
tAl
dAl
10,000
8,000
6,000
4,000
2,000
0
Concentration (µg/L)
ANZECC 80%
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site

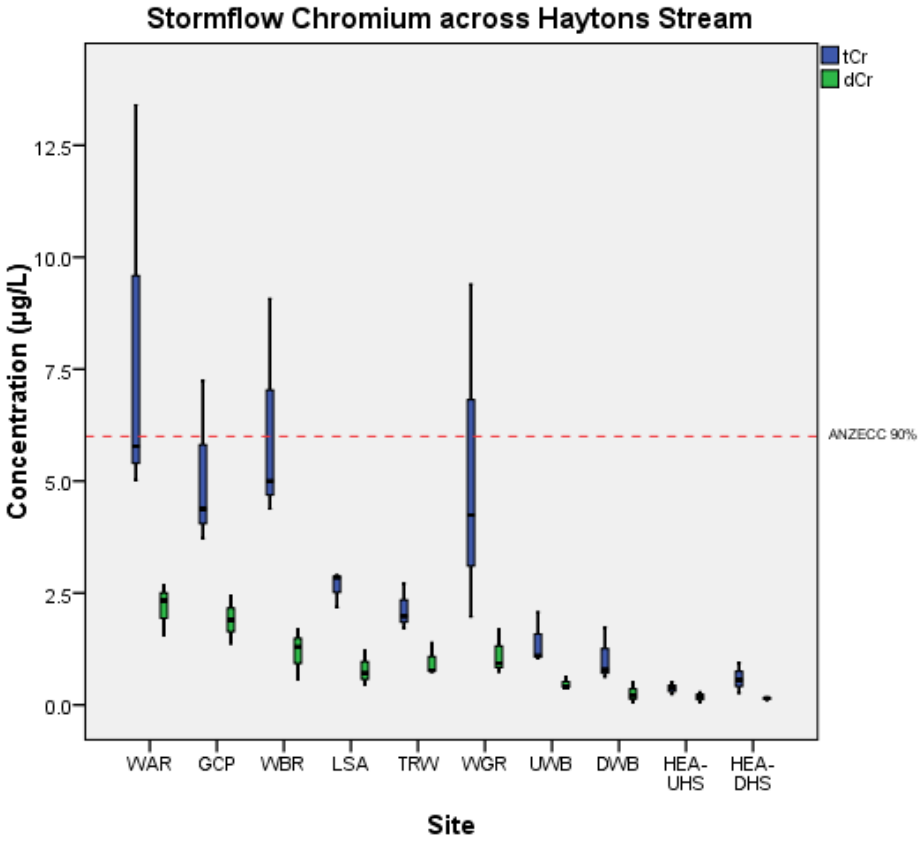

Baseflow Arsenic across Haytons Stream
tAs
dAs
Concentration (µg/L)
0
1
2
3
4
ANZECC 99%
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site

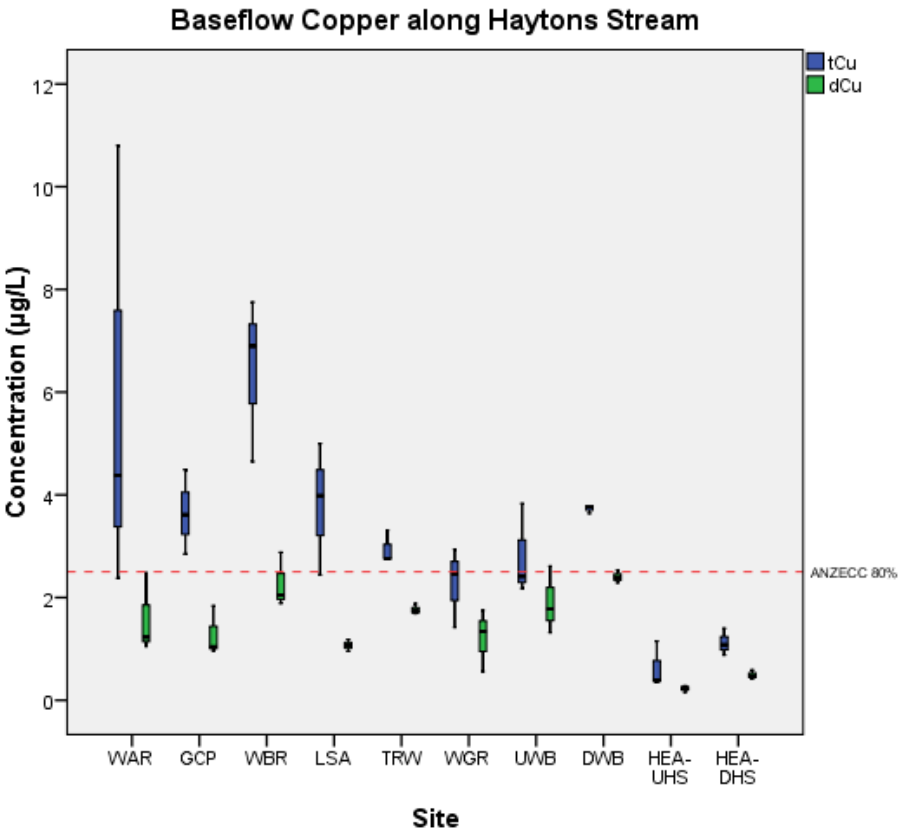

Stormflow Arsenic across Haytons Stream
tAs
dAs
Concentration (µg/L)
0
1
2
3
4
5
6
ANZECC 99%
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site

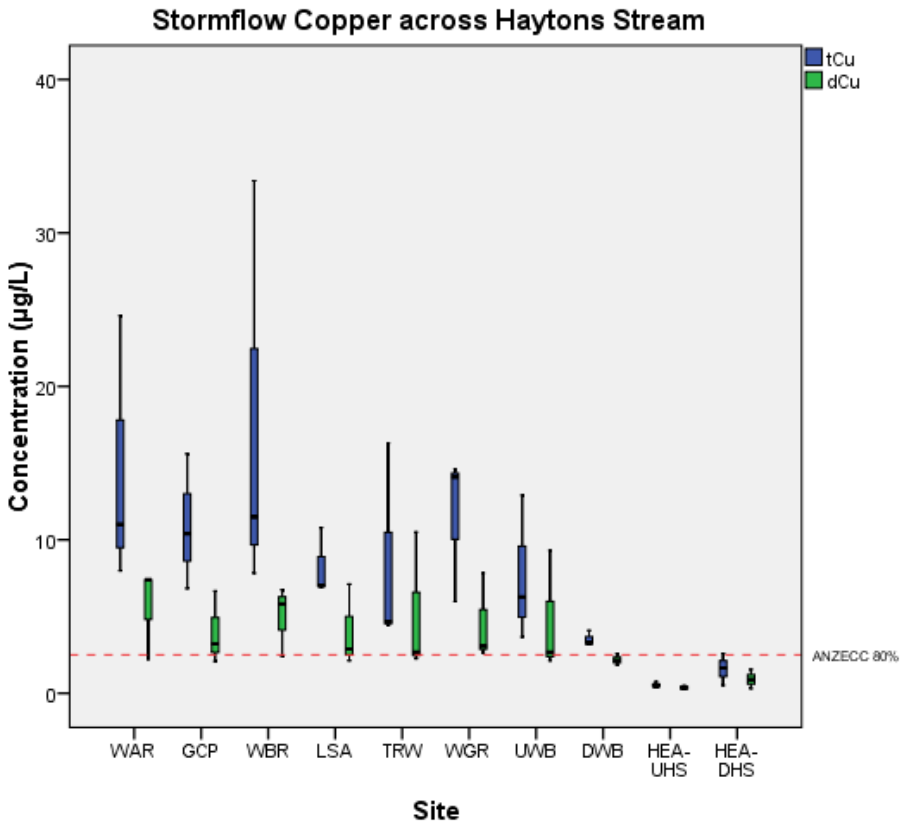

Baseflow Cadmium across Haytons Stream
*2.25 µg/L
*1.09 µg/L
*7.28 µg/L
tCd
dCd
ANZECC 80%
ANZECC 90%
Concentration (µg/L)
1.0
0.8
0.6
0.4
0.2
0.0
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site

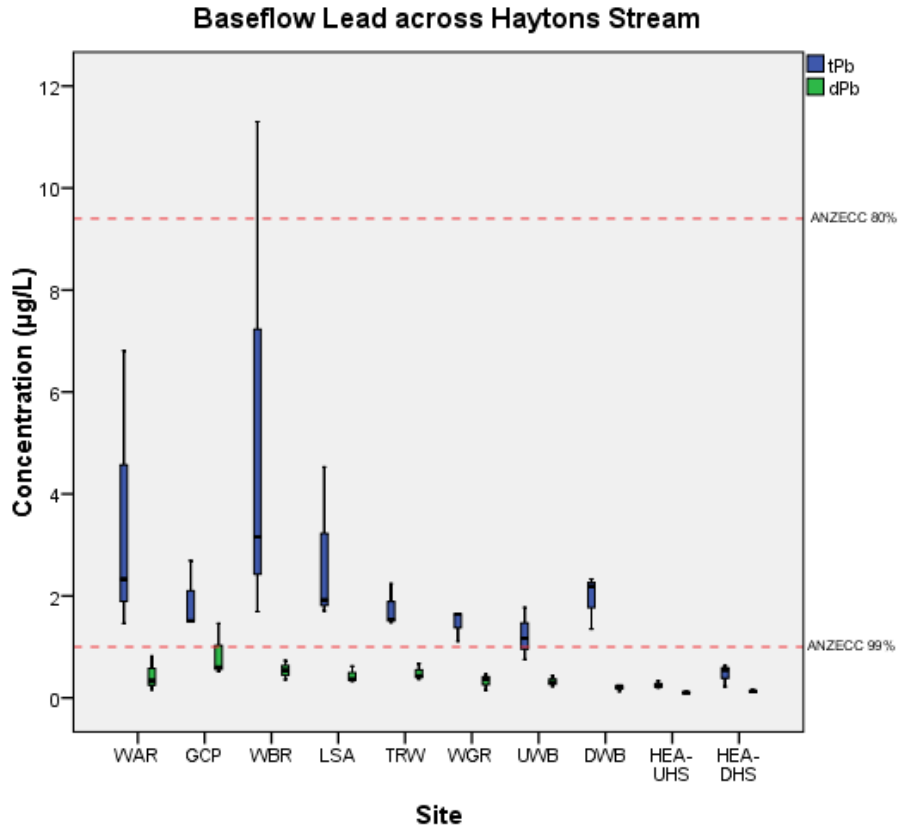

Stormflow Cadmium across Haytons Stream
*221 µg/L
*6.08 µg/L
*6.05 µg/L
*3.44 µg/L
*2.92 µg/L
tCd
dCd
ANZECC 80%
ANZECC 99%
Concentration (µg/L)
1.0
0.8
0.6
0.4
0.2
0.0
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site

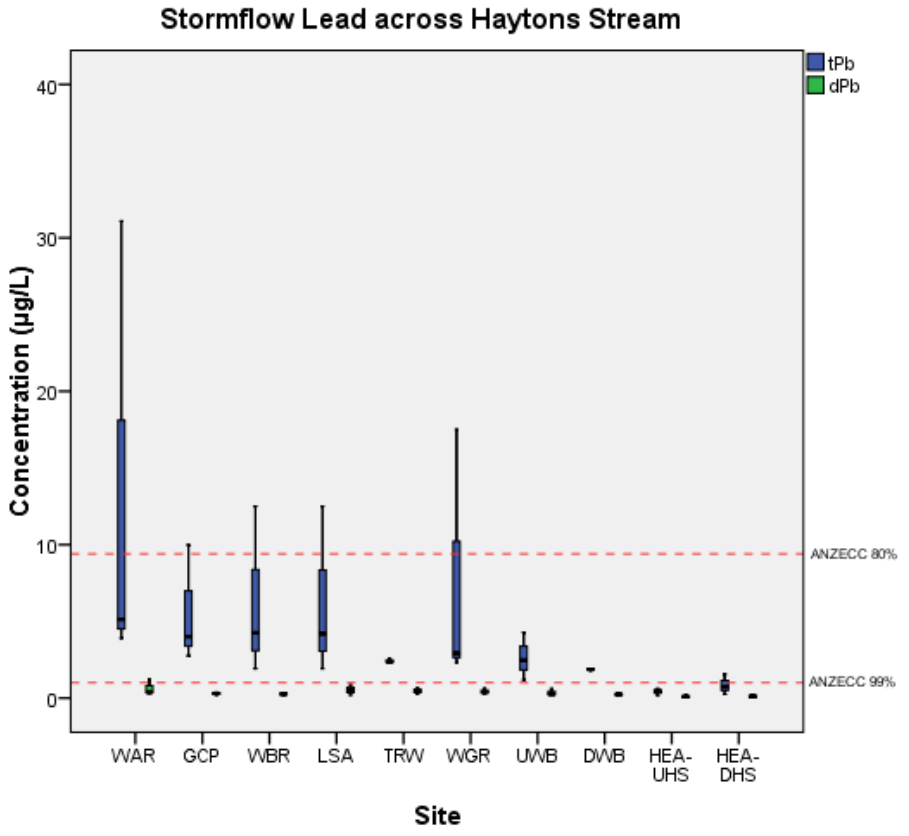

Baseflow Chromium across Haytons Stream
tCr
dCr
Concentration (µg/L)
25
20
15
10
5
0
ANZECC 90%
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site

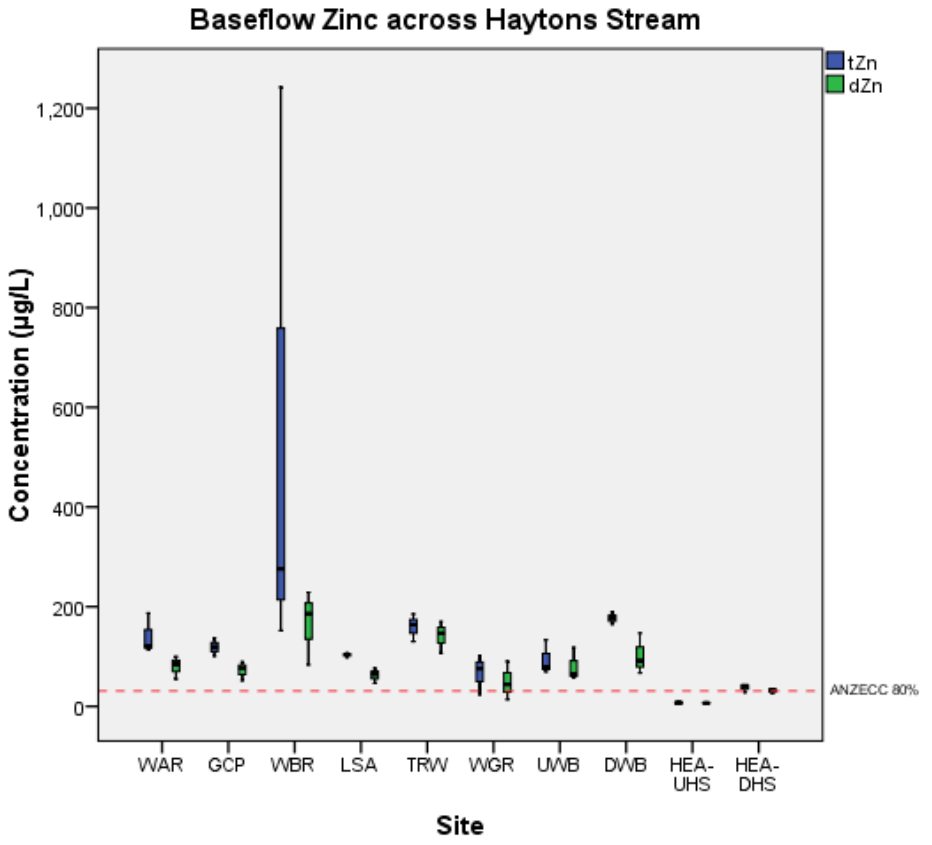

Stormflow Chromium across Haytons Stream
tCr
dCr
Concentration (µg/L)
12.5
10.0
7.5
5.0
2.5
0.0
ANZECC 90%
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site


Baseflow Copper along Haytons Stream
tCu
dCu
Concentration (µg/L)
12
10
8
6
4
2
0
ANZECC 80%
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site


Stormflow Copper across Haytons Stream
tCu
dCu
Concentration (µg/L)
40
30
20
10
0
ANZECC 80%
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site


Baseflow Lead across Haytons Stream
tPb
dPb
ANZECC 80%
ANZECC 99%
Concentration (µg/L)
0
2
4
6
8
10
12
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site


Stormflow Lead across Haytons Stream
tPb
dPb
ANZECC 80%
ANZECC 99%
Concentration (µg/L)
0
10
20
30
40
WAR
GCP
WBR
LSA
TRW
WGR
UWB
DWB
HEA-UHS
HEA-DHS
Site



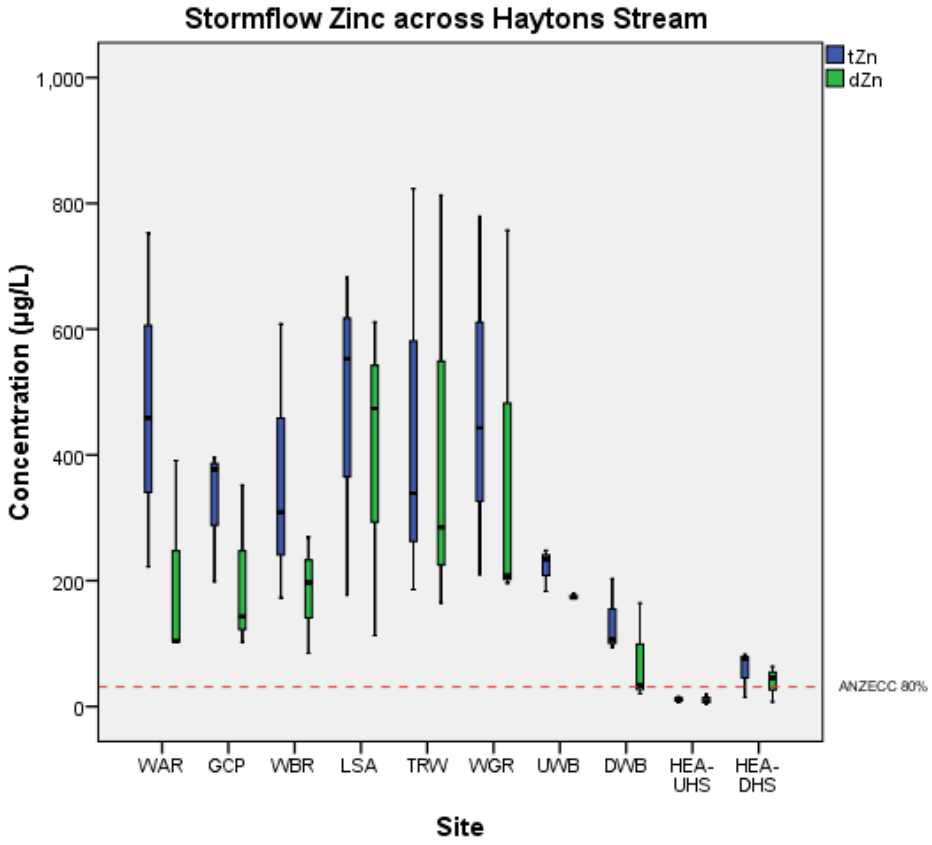
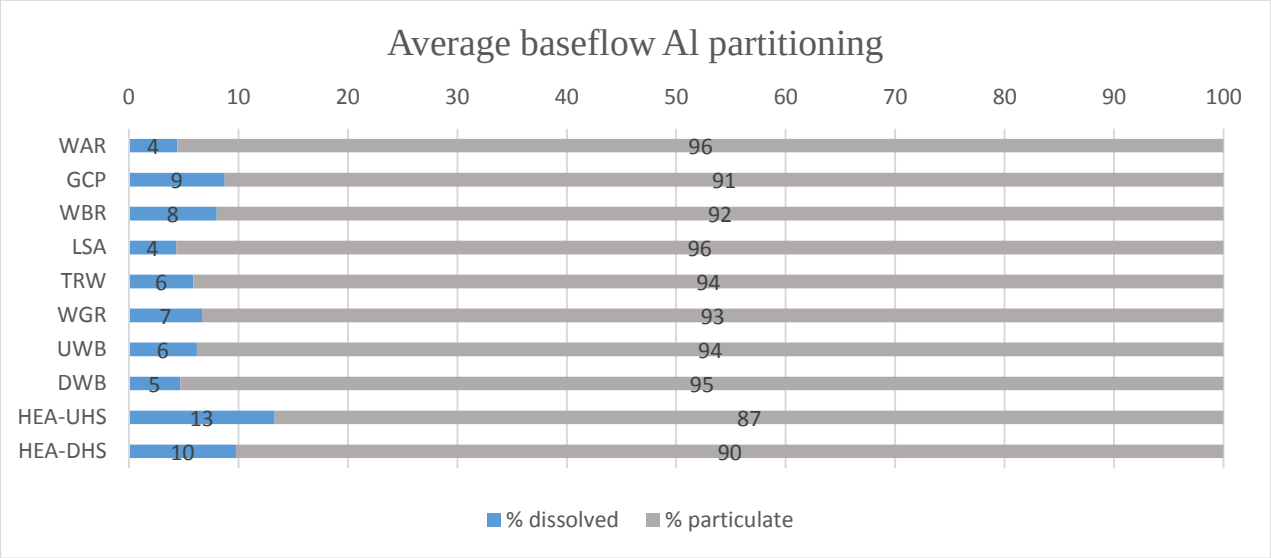
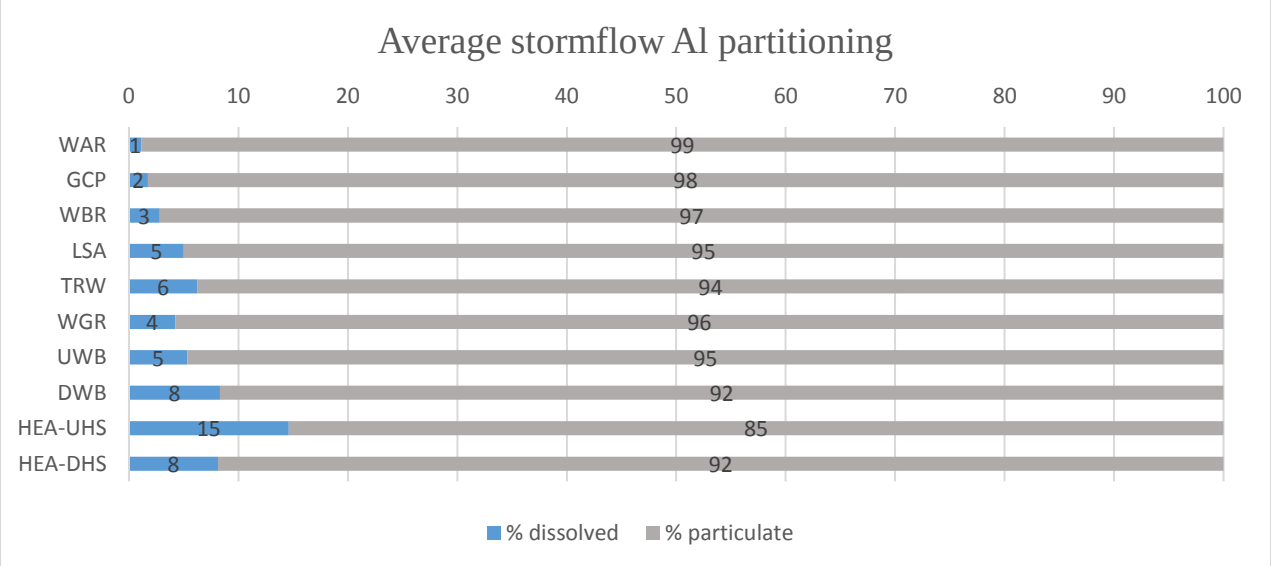


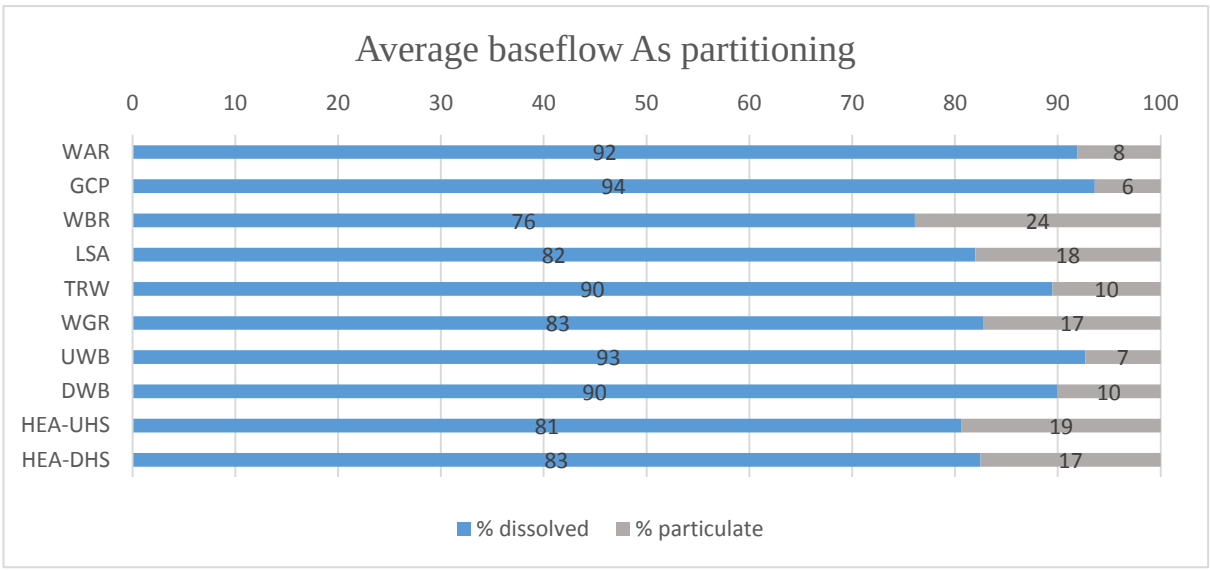
Figure 3.5 Baseflow and stormflow metal concentrations throughout Haytons Stream

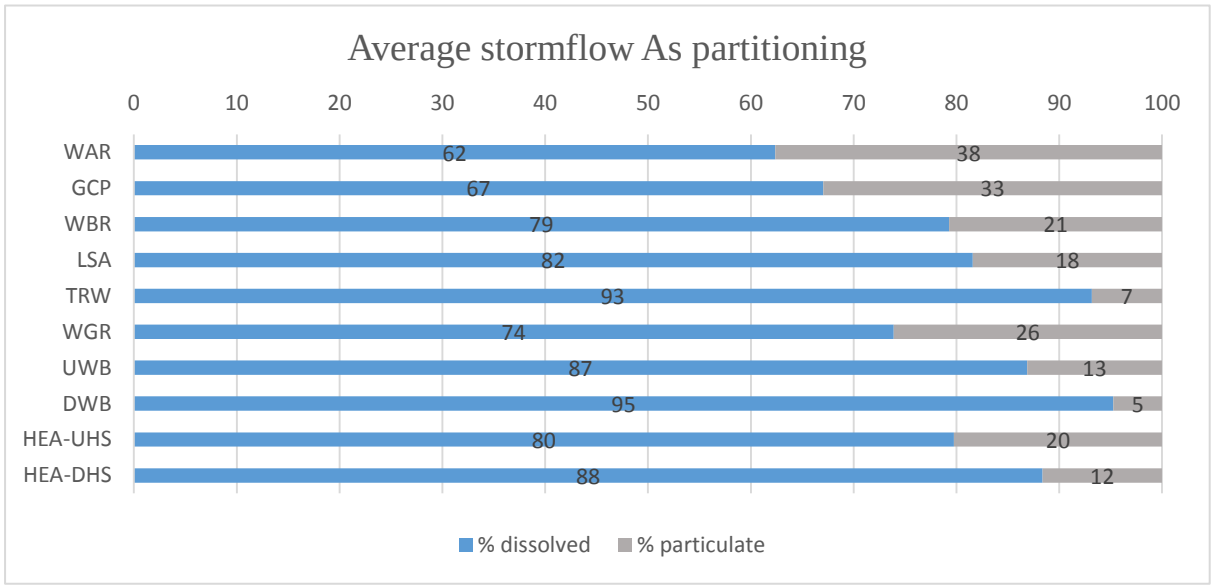
Partitioning

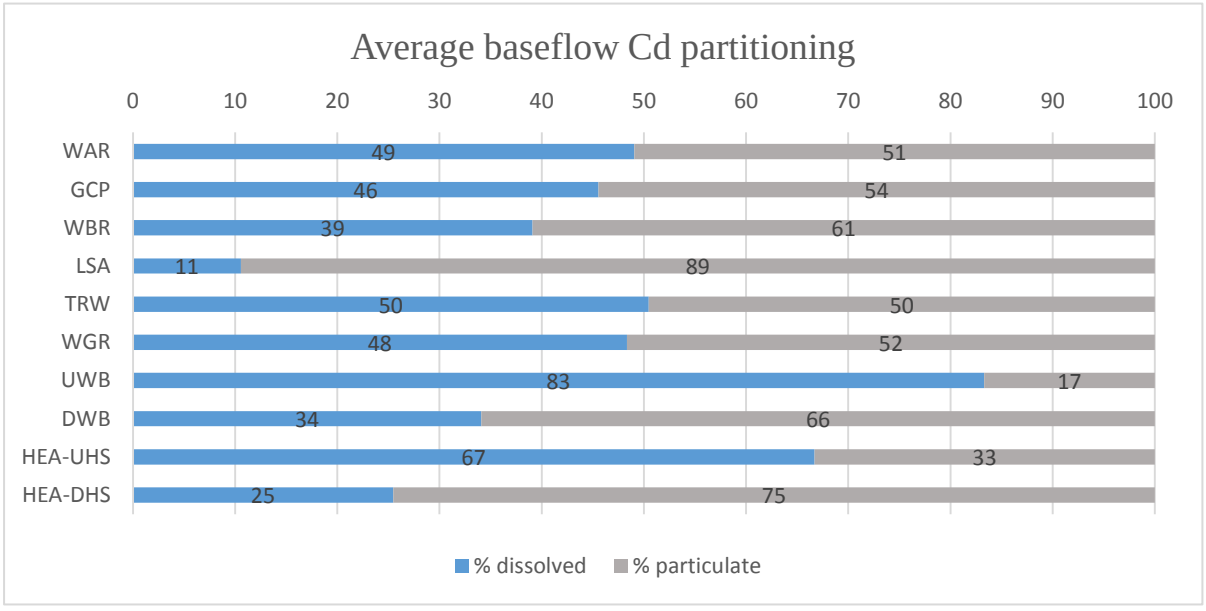
Partitioning (for dissolved and particulate metals) was calculated for the above metals exceeding ANZECC guidelines, showing the average percentages of particulate and dissolved form over the three baseflow and three stormflow events (Figure 3.6). Average total and dissolved metal concentrations from each site were taken, and divided to calculate the percentage dissolved metal present and subsequent percentage particulate metal.

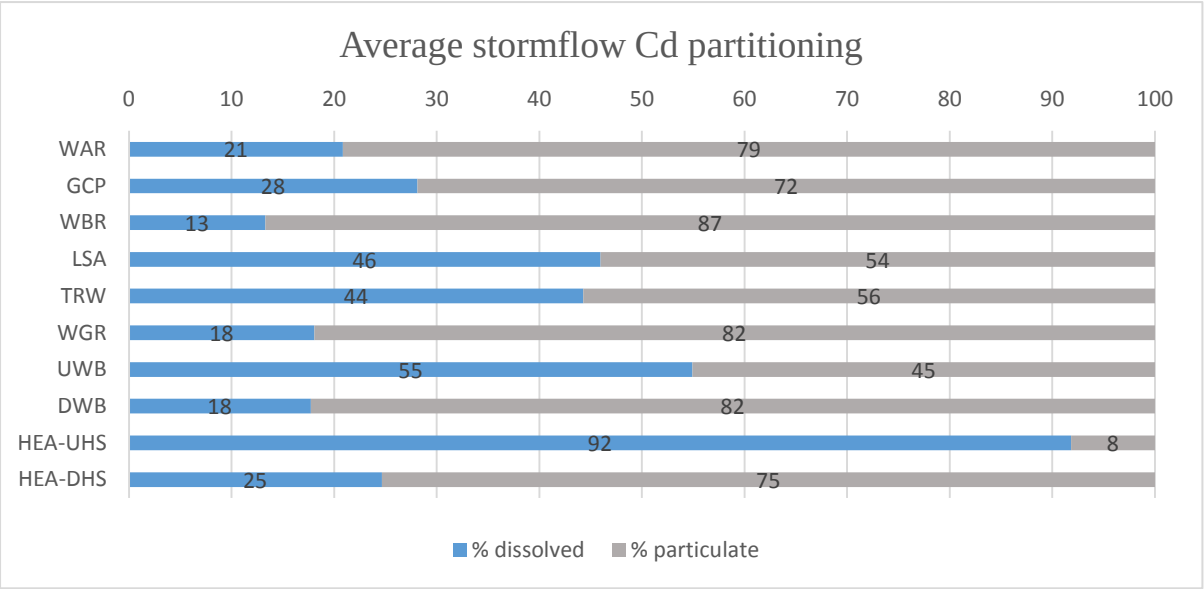


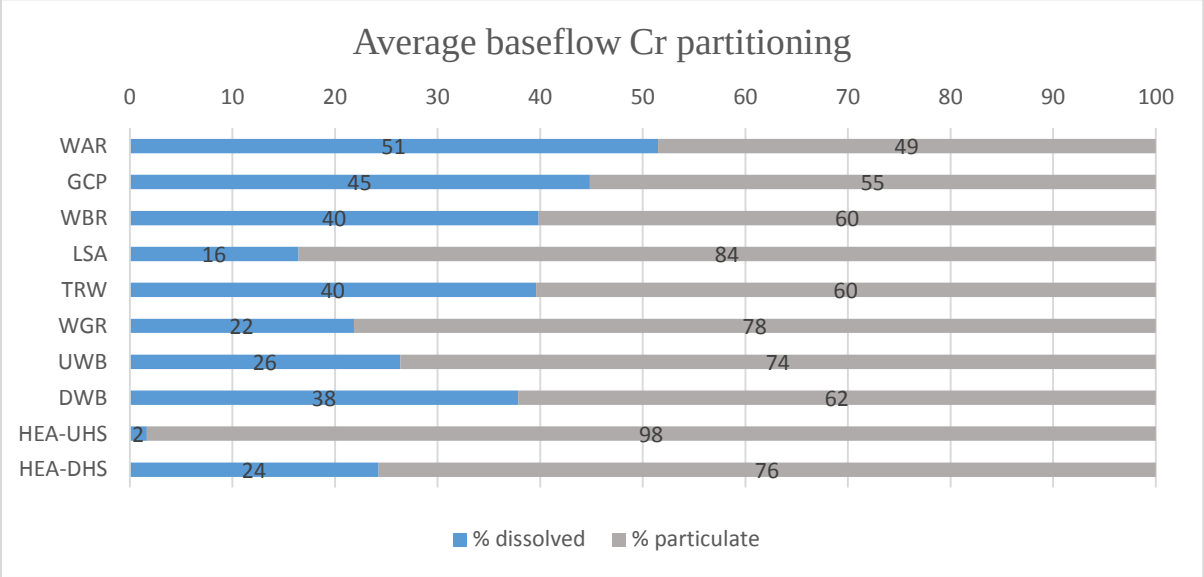


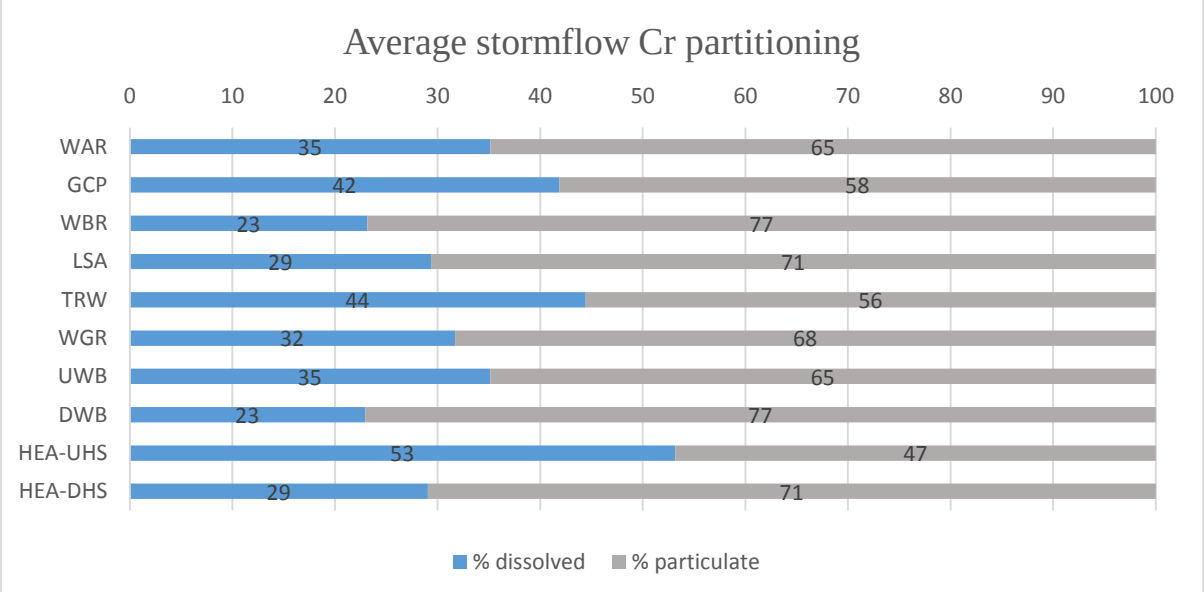

Average baseflow As partitioning
0 10 20 30 40 50 60 70 80 90 100
WAR 92 8
GCP 94 6
WBR 76 24
LSA 82 18
TRW 90 10
WGR 83 17
UWB 93 7
DWB 90 10
HEA-UHS 81 19
HEA-DHS 83 17
% dissolved
% particulate

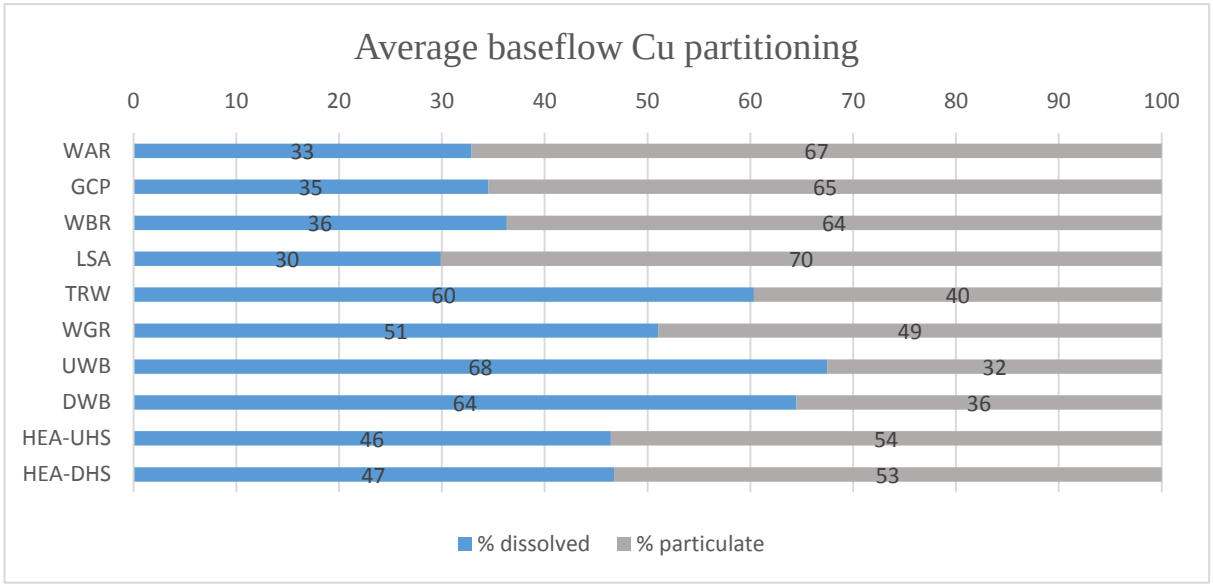

Average stormflow As partitioning
0 10 20 30 40 50 60 70 80 90 100
WAR 62 38
GCP 67 33
WBR 79 21
LSA 82 18
TRW 93 7
WGR 74 26
UWB 87 13
DWB 95 5
HEA-UHS 80 20
HEA-DHS 88 12
% dissolved
% particulate

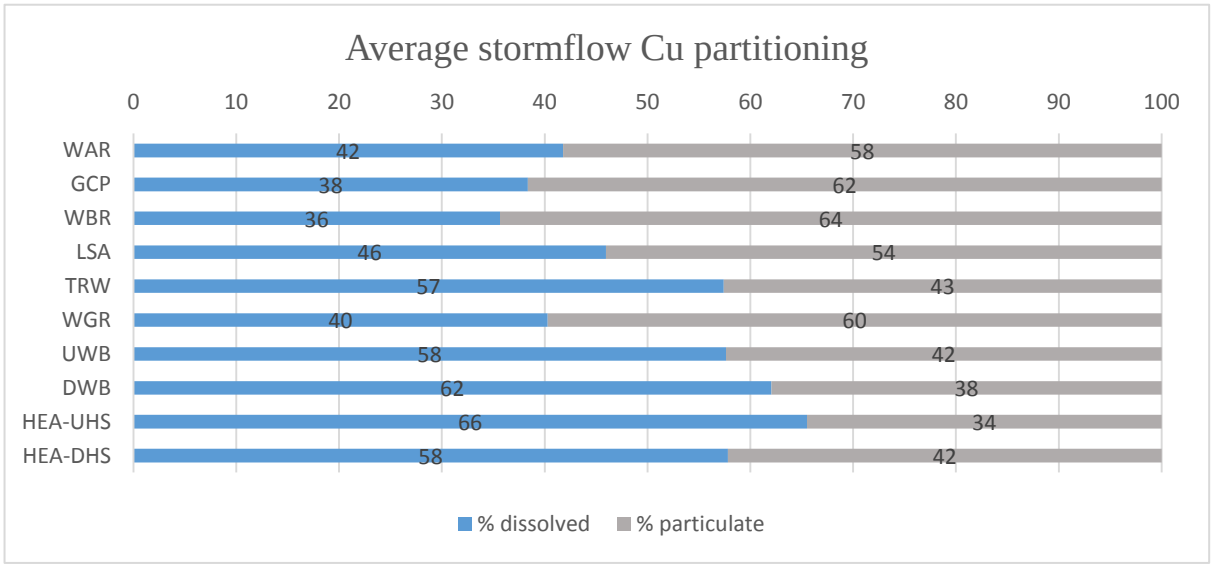

Average baseflow Cd partitioning
0 10 20 30 40 50 60 70 80 90 100
WAR 49 51
GCP 46 54
WBR 39 61
LSA 11 89
TRW 50 50
WGR 48 52
UWB 83 17
DWB 34 66
HEA-UHS 67 33
HEA-DHS 25 75
% dissolved
% particulate

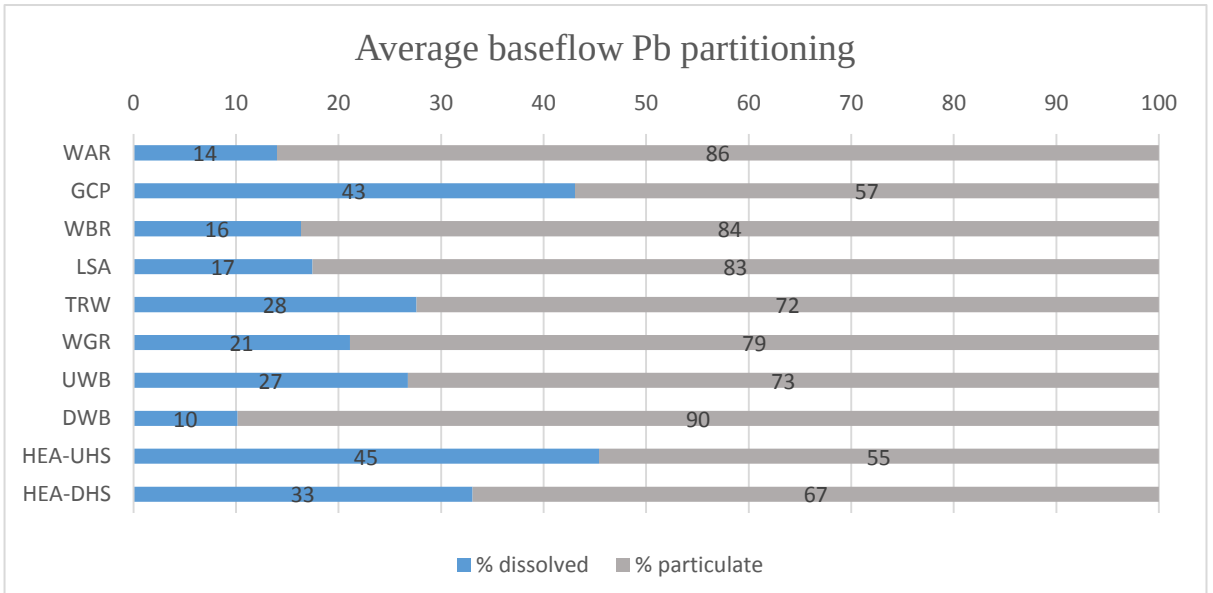

Average stormflow Cd partitioning
0 10 20 30 40 50 60 70 80 90 100
WAR 21 79
GCP 28 72
WBR 13 87
LSA 46 54
TRW 44 56
WGR 18 82
UWB 55 45
DWB 18 82
HEA-UHS 92 8
HEA-DHS 25 75
% dissolved
% particulate

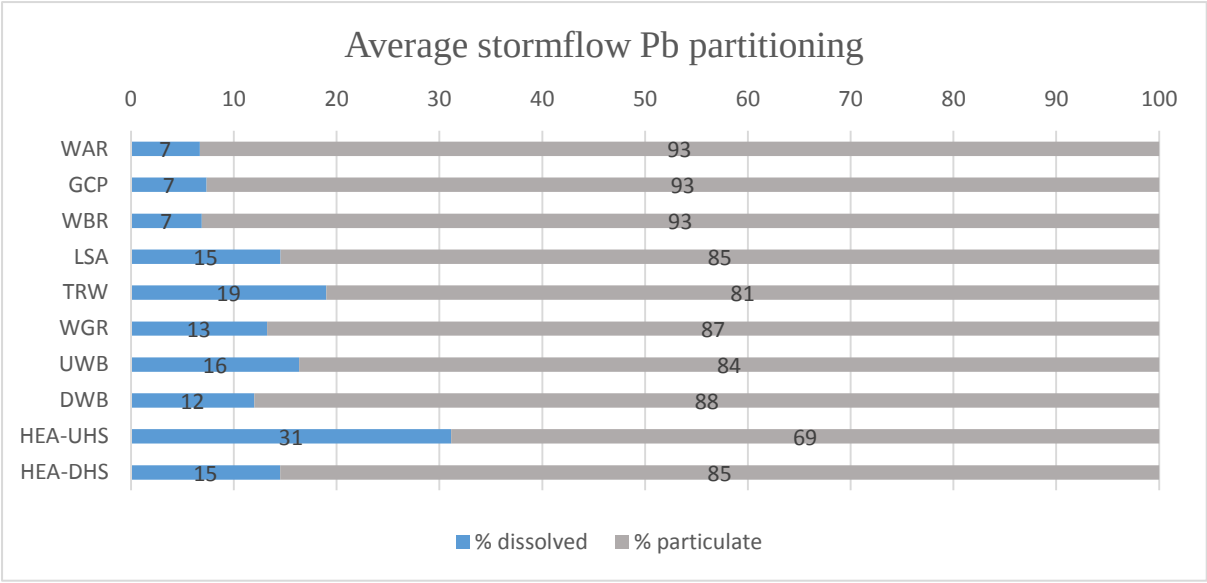

Average baseflow Cr partitioning
0 10 20 30 40 50 60 70 80 90 100
WAR 51 49
GCP 45 55
WBR 40 60
LSA 16 84
TRW 40 60
WGR 22 78
UWB 26 74
DWB 38 62
HEA-UHS 2 98
HEA-DHS 24 76
% dissolved
% particulate

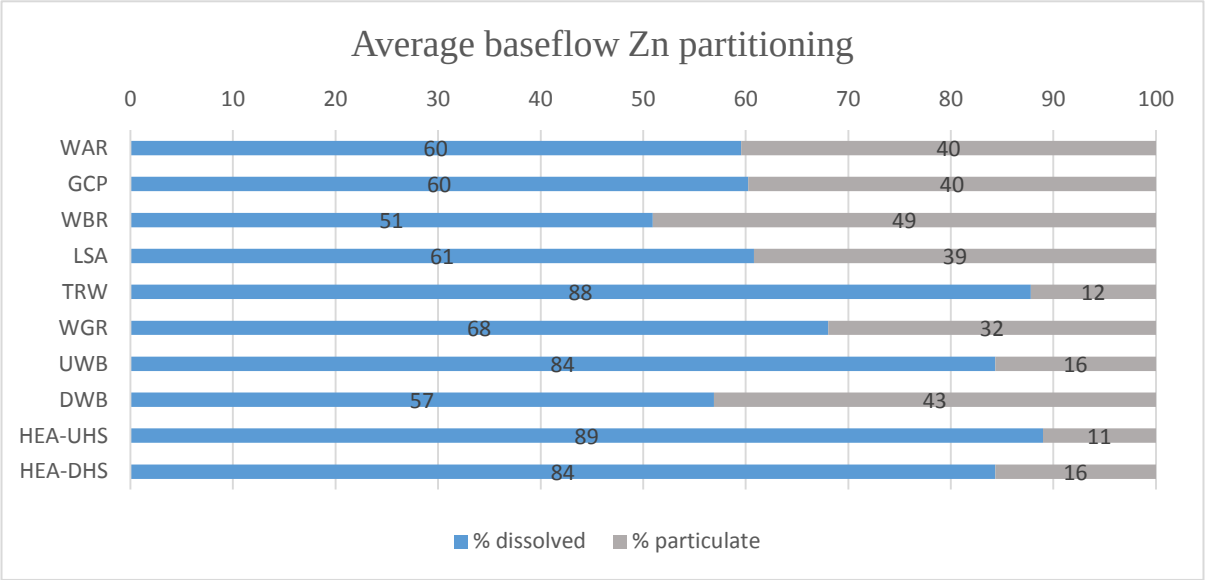

Average stormflow Cr partitioning
0 10 20 30 40 50 60 70 80 90 100
WAR 35 65
GCP 42 58
WBR 23 77
LSA 29 71
TRW 44 56
WGR 32 68
UWB 35 65
DWB 23 77
HEA-UHS 53 47
HEA-DHS 29 71
% dissolved
% particulate


Average baseflow Cu partitioning
0 10 20 30 40 50 60 70 80 90 100
WAR 33 67
GCP 35 65
WBR 36 64
LSA 30 70
TRW 60 40
WGR 51 49
UWB 68 32
DWB 64 36
HEA-UHS 46 54
HEA-DHS 47 53
% dissolved
% particulate


Average stormflow Cu partitioning
0 10 20 30 40 50 60 70 80 90 100
WAR 42 58
GCP 38 62
WBR 36 64
LSA 46 54
TRW 57 43
WGR 40 60
UWB 58 42
DWB 62 38
HEA-UHS 66 34
HEA-DHS 58 42
% dissolved
% particulate


Average baseflow Pb partitioning
0 10 20 30 40 50 60 70 80 90 100
WAR 14 86
GCP 43 57
WBR 16 84
LSA 17 83
TRW 28 72
WGR 21 79
UWB 27 73
DWB 10 90
HEA-UHS 45 55
HEA-DHS 33 67
% dissolved
% particulate





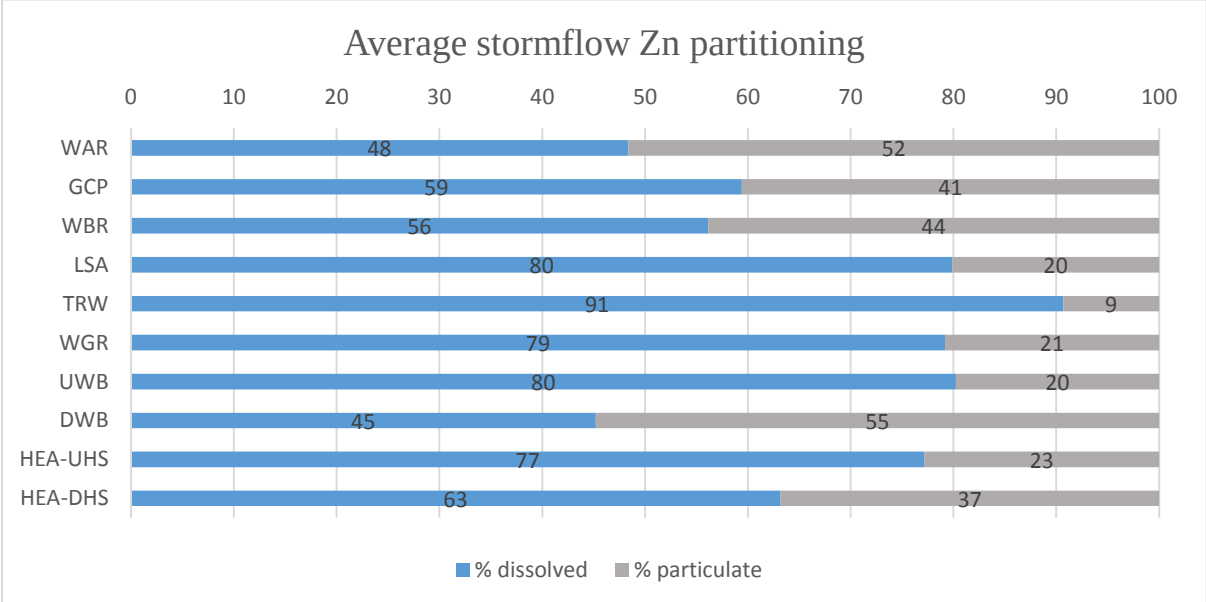


Figure 3.6 Baseflow and stormflow metal partitioning throughout Haytons Stream

Trace element statistics

Differences in trace element concentrations between key sites, between baseflow and stormflow, and between the industrial upper land use and lower pastoral/ re-landscaped land use sites were determined (Tables 3.5 and 3.6). Stormflow conditions generated significantly higher concentrations of a number of trace elements (As, Cd, Cu, Ni, Pb and Zn) when compared to baseflow, for both total and dissolved fractions. There were statistically significant differences in concentrations (for total Al, dissolved Cu and total and dissolved Zn) downstream of Haytons Stream on the Heathcote River when compared to upstream of the confluence, indicating Haytons Stream is a source of these metals to the downstream Heathcote River. Although there were evident differences in concentration between UWB and DWB, with frequent baseflow metal exports out of the basin and into the Heathcote River (indicating the basin is poor in removing metals- see Appendix 4 for further UWB/ DWB concentrations), the differences in concentration were not statistically significant.

Table 3.5 T-tests conducted and significant differences between metals in Haytons Stream

	Trace elements[4]								
		Al	As	Cd	Cr	Cu	Ni	Pb	Zn
T-Tests	Baseflow vs stormflow total metals		***	*			*	*	**
	Baseflow vs Stormflow dissolved metals		**	*		*			**
	Upstream Wigram Basin vs Downstream Wigram Basin total metals								
	Upstream Wigram Basin vs Downstream Wigram Basin dissolved metals								
	Heathcote U/S vs Heathcote D/s total metals	*							*
	Heathcote U/S vs Heathcote D/S dissolved metals					*			***

[4] * $p < 0.05$

** $p < 0.01$

*** $p < 0.001$

When comparing the industrial upper catchment (sites 1-4) and the lower pastoral/ re-landscaped catchment (sites 5-8), the upper catchment had significantly higher concentrations of numerous metals (Al, Cr, Cu, Ni and Pb) compared to the lower catchment (Table 3.6). This occurred during both baseflow and stormflow events, and for both total and dissolved metals, indicating that the industrial land use and subsequent activities that occur within the catchment are a significant source of metals to Haytons Stream at all times. Zinc was not significantly different between the land uses, and was found at elevated concentrations at all sampling sites across the catchment as seen above.

Table 3.6 Upper catchment vs lower catchment t-test significant differences between metals in Haytons Stream

Trace elements									
		Al	As	Cd	Cr	Cu	Ni	Pb	Zn
T-tests	Baseflow total metals Lower vs Upper catchment					**	*	*	
	Baseflow dissolved metals Lower vs Upper catchment				*		**	*	
	Stormflow total metals Lower vs Upper catchment	*			*	*		*	
	Stormflow dissolved metals Lower vs Upper catchment				**				

Average baseflow dissolved metal concentrations across Haytons Stream were used in a Pearson correlation with bioavailable sediment concentrations, to interpret if they increase together across the catchment and suggest the sediment is a source to the water column. The metals Cd, Cu and Pb had correlations of 0.71 ($p < 0.02$), 0.75 ($p < 0.01$) and 0.72 ($p < 0.01$), suggesting somewhat strong increases together. However, Zn had a dissolved metal- bioavailable sediment correlation of 0.86 ($p < 0.001$), suggesting a very strong correlation. This can further explain why dissolved Zn concentrations are elevated in baseflow, with labile metals from sediment a likely source to the water column.

3.3.2.4 Nutrients

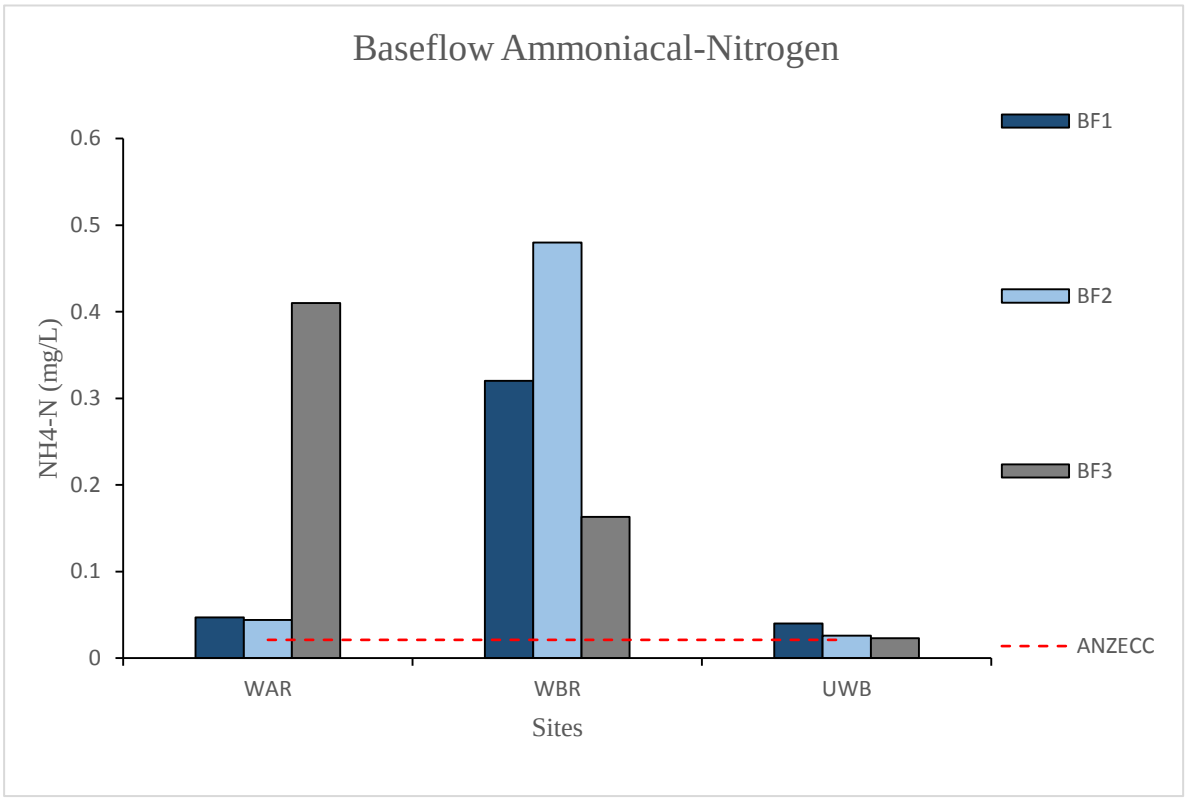
During baseflow and stormflow ammoniacal-nitrogen, dissolved reactive phosphorous and nitrate-nitrite nitrogen were all highest at WBR. Sampling site UWB commonly had the lowest concentrations of all nutrients. Baseflow and stormflow averages (in bold) and ranges for nutrients are presented in Table 3.7 below. Concentrations of A-N and DRP were higher in stormflow, with maximum concentrations of 13.5 mg/L A-N and 4 mg/L DRP found at WBR. NNN concentrations were lower in stormflow at all sites compared to baseflow concentrations.

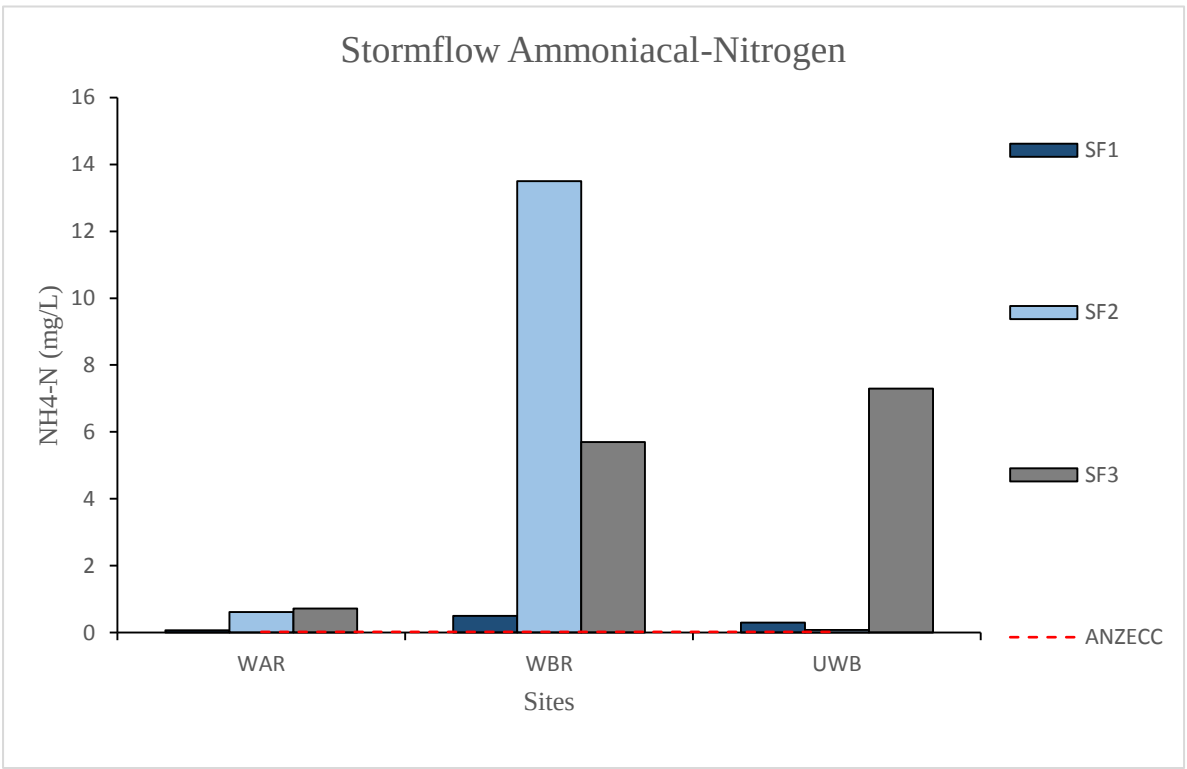
Significant differences existed in baseflow ammoniacal-N between WBR and UWB (p = 0.007), whereas WBR and UWB also had significantly different NNN concentrations during baseflow (p =0.02). DRP had the most significant differences; between WAR and WBR in baseflow and stormflow (p = 0.007 and 0.02 respectively) and between WBR and UWB during baseflow (p = 0.009) and stormflow (p = 0.01). Overall ammoniacal-N for all of Haytons Stream was significantly different between baseflow and stormflow events (p = 0.01).

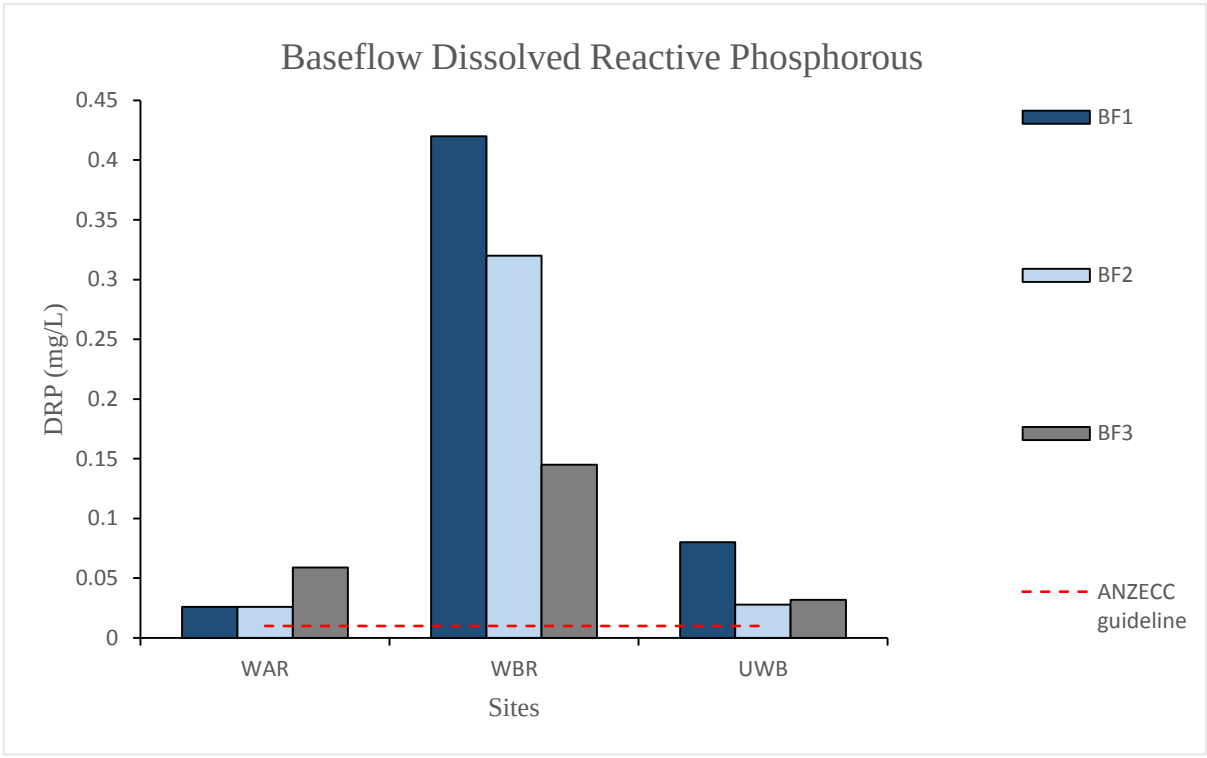
Using pH-adjusted ammonia trigger values, WBR had ammoniacal-N concentrations exceeding the 95% species protection during stormflow two and stormflow three, and UWB had an exceedance during stormflow three. Baseflow and stormflow graphs of all sampled nutrients, compared to applicable ANZECC trigger values are presented in Figure 3.7.

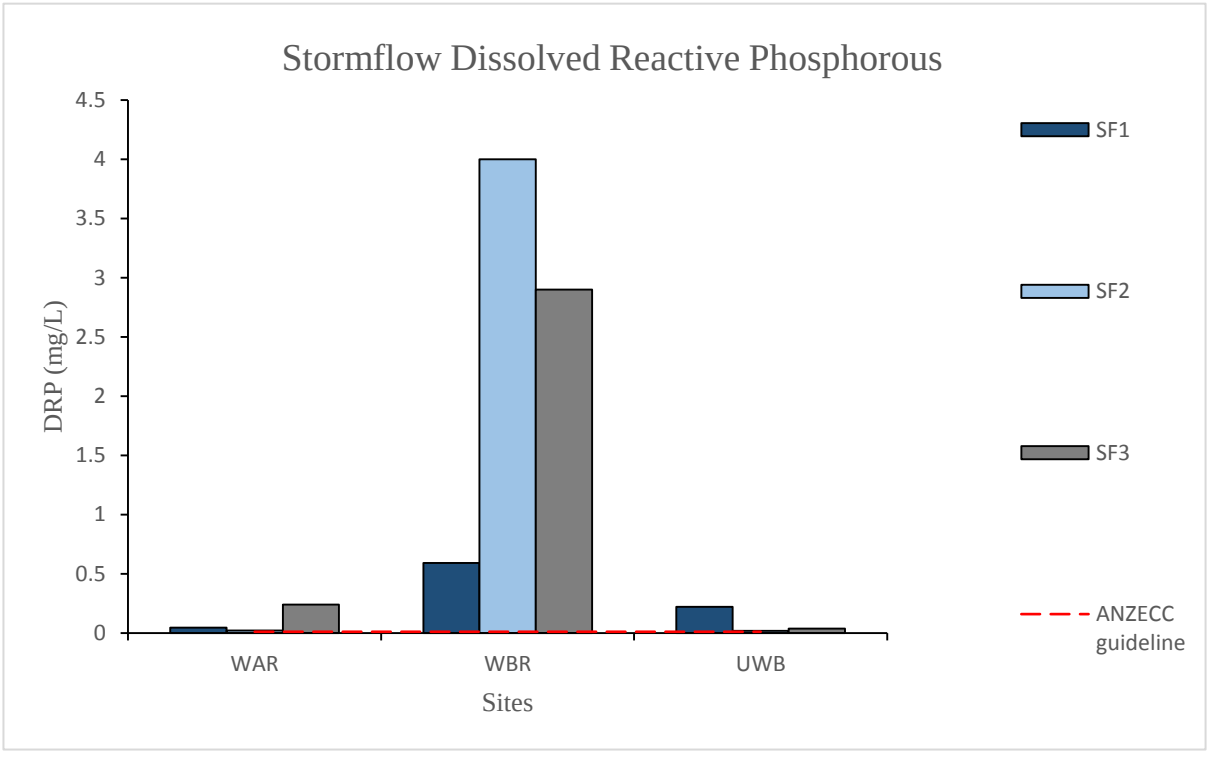
Table 3.7 Baseflow and stormflow nutrient concentrations throughout Haytons Stream

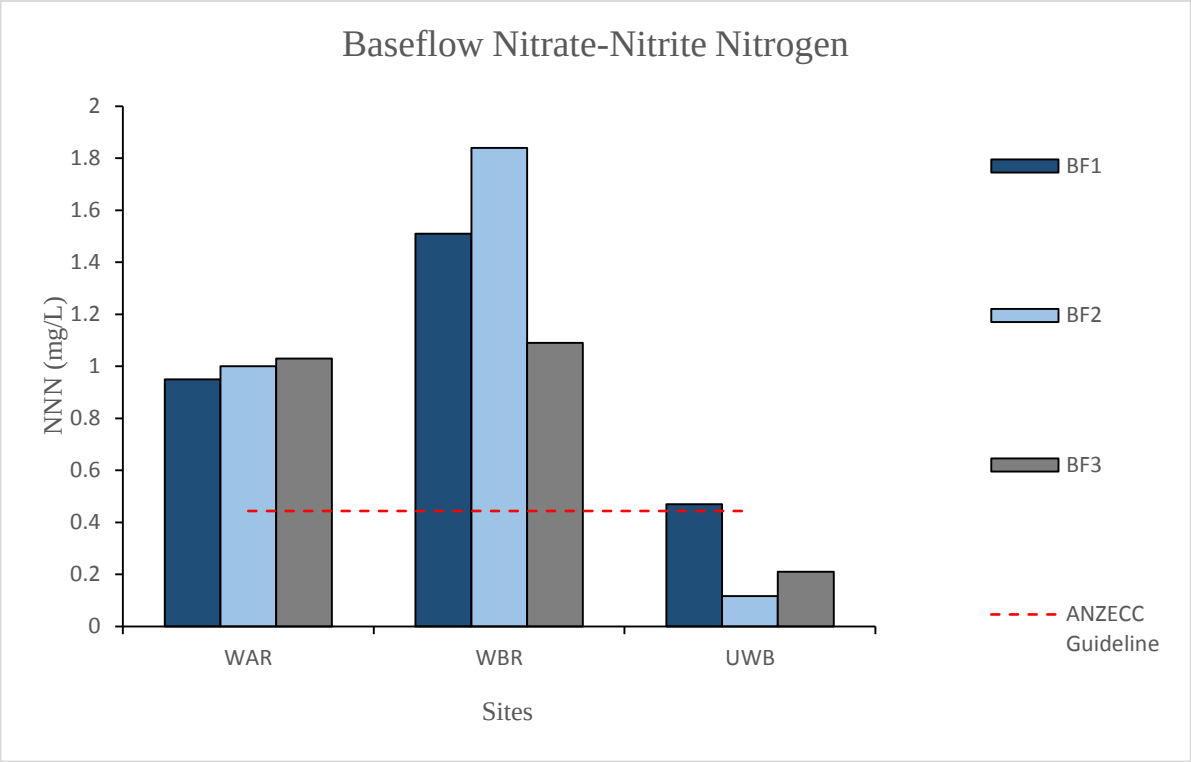
Baseflow			
Site	A-N (mg/L)	DRP (mg/L)	NNN (mg/L)
WAR	**0.17** (0.04 -0.41)	**0.04** (0.03 -0.06)	**0.99** (0.95 -1.03)
WBR	**0.32** (0.16 -0.48)	**0.30** (0.15 -0.42)	**1.48** (1.09 -1.84)
UWB	**0.03** (0.02 -0.04)	**0.05** (0.03 -0.08)	**0.27** (0.12 -0.47)
Stormflow			
WAR	**0.47** (0.07 -0.42)	**0.10** (0.02 -0.24)	**0.44** (0.08 -0.76)
WBR	**6.57** (0.5 -13.5)	**2.50** (0.59 -4)	**0.76** (0.13 -1.23)
UWB	**2.56** (0.08 -7.3)	**0.09** (0.02 -0.22)	**0.28** (0.12 -0.43)


Baseflow Ammoniacal-Nitrogen
NH4-N (mg/L)
0.6
0.5
0.4
0.3
0.2
0.1
0
WAR
WBR
UWB
Sites
BF1
BF2
BF3
ANZECC


Stormflow Ammoniacal-Nitrogen
NH4-N (mg/L)
16
14
12
10
8
6
4
2
0
WAR
WBR
UWB
Sites
SF1
SF2
SF3
ANZECC


Baseflow Dissolved Reactive Phosphorous
DRP (mg/L)
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
WAR
WBR
UWB
Sites
BF1
BF2
BF3
ANZECC guideline


Stormflow Dissolved Reactive Phosphorous
DRP (mg/L)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
WAR
WBR
UWB
Sites
SF1
SF2
SF3
ANZECC guideline



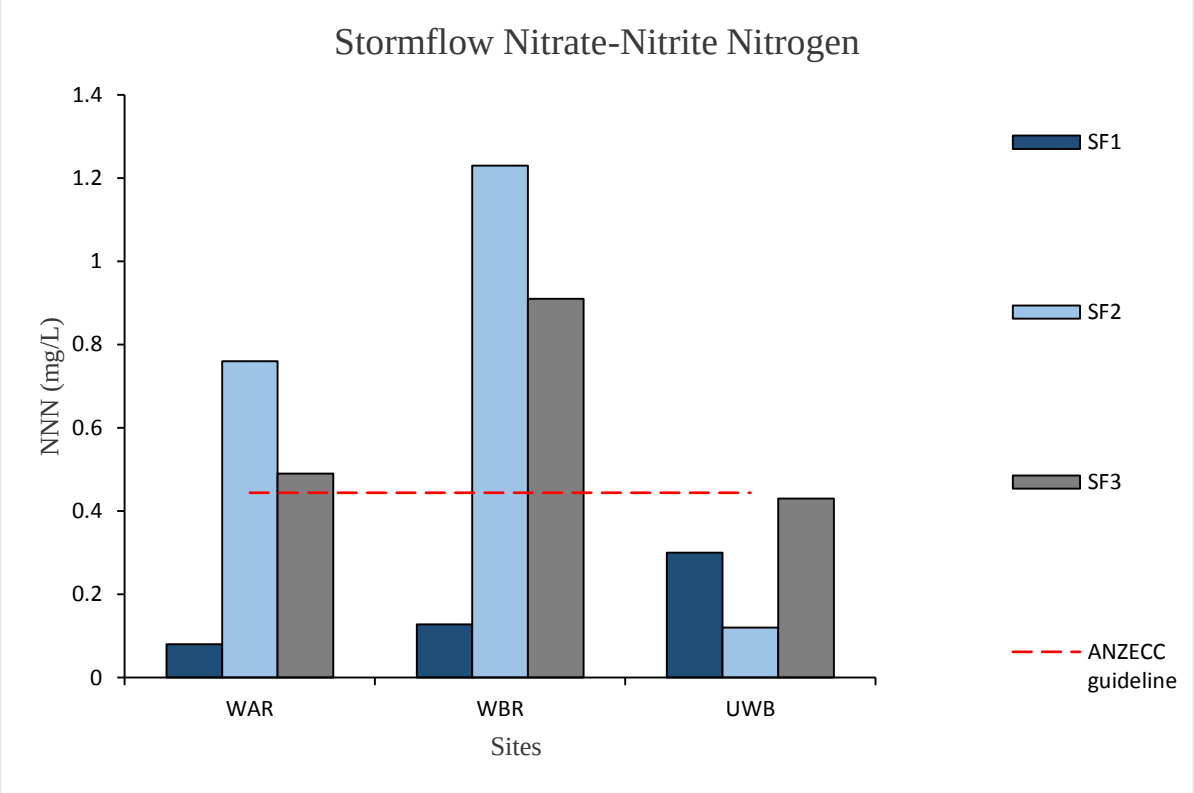


Figure 3.7 Nutrient concentrations across Haytons Stream

3.3.2.5 E. coli

Average *E. coli* concentrations during baseflow were similar at the three sampled sites, with mean concentrations of 32, 69 and 31 MPN/100 ml at WAR, WBR and UWB respectively. No sample during any dry weather run exceeded the NRRP guideline of 550 MPN/100 ml for the water quality class 'spring-fed- plains- urban'. The highest single baseflow concentration was 120 MPN/100 ml at WBR, and the lowest baseflow concentration was 12 MPN/100 ml at UWB. There were no statistically significant differences in *E. coli* between any sites in dry weather. *E. coli* concentrations were substantially higher during stormflow, with all but one sample exceeding the 550 MPN/100 ml guideline. Sampling sites regularly exceeded the Hill Laboratories concentration limit of Most Probable Number counts (therefore reported as >2420 MPN/100 ml) during stormflow conditions. As stormflow concentrations were often reported back as >2420 MPN/100 ml, statistical analysis could not be conducted for wet weather concentrations. All sampled *E. coli* concentrations are presented in Table 3.8 below. Values in bold are in exceedance of the NRRP/ LWRP guideline for urban streams.

Table 3.8 Baseflow and stormflow E. coli concentrations throughout Haytons Stream

E. coli concentrations (MPN/100 ml)						
Site	Baseflow 1	Baseflow 2	Baseflow 3	Stormflow 1	Stormflow 2	Stormflow 3
WAR	16	18	61	**1414**	**>2420**	**1300**
WBR	61	120	25	**727**	**>2420**	**2420**
UWB	47	35	12	**>2420**	**921**	548

3.3.2.6 Reactive discharge sampling

As part of understanding and quantifying contaminant discharges to Haytons Stream, if a pipe discharge in dry weather or a slick/ scum on the stream surface was observed, a sample was taken and sent to Hill Laboratories to increase knowledge of what and where contaminants are being discharged across the catchment. Twelve separate discharge events were observed (stars indicate the same pipe), ranging from instream hydrocarbon slicks/ scums to visible pipe discharges into the stream, at three separate locations across the catchment (Table 3.9). The separate locations in the catchment where discharges were found are discussed below.

Table 3.9 'Discharges' found in the Haytons Stream catchment between 23/5 – 27/9

Discharge captured	Location	Date	A-N (mg/L)	DRP (mg/L)	NNN (mg/L)	*E. coli* (MPN/100 ml)	∑ PAHs (µg/L)	∑ TPHs (mg/L)
Hydrocarbon slick	Waterloo Rd	23/5	-	-	-	-	0.137	-
Hydrocarbon slick	Waterloo Rd	16/6	-	-	-	-	0.21	-
Hydrocarbon slick	Waterloo Rd	7/7	-	-	-	-	-	-
Sticky hydrocarbon slick	Waterloo Rd	25/7	0.137	0.44	1.01	147	-	13.1
Hydrocarbon slick	Waterloo Rd	18/8	-	-	-	-	-	<0.7
Milky opaque stream colour	Waterloo Rd	30/8	0.66	0.033	22	-	-	-
Organic yellow scum	Waterloo Rd	30/8	-	-	-	>1600	-	-
Pipe discharge*	Washbournes Rd	5/5	0.47	0.114	0.71	11	-	-
Pipe discharge*	Washbournes Rd	29/5	0.078	0.094	0.98	4	-	-
Pipe discharge	Washbournes Rd	8/9	0.71	0.131	0.98	<1	-	-
Pipe discharge	Gerald Connolly Place	25/7	1.54	0.059	0.51	4	-	2
Shiny sewage-smelling scum	Gerald Connolly Place	27/9	0.096	0.04	0.21	517	-	-

Waterloo Road

The majority of discharges were observed at Waterloo Road, where the stream immediately exits the stormwater network. All discharges at this site were seen exiting the large pipe, which drains the whole upper catchment of industrial Hornby (Figure 3.8). Almost all discharges at this site were hydrocarbon-based slicks exiting from the network, with the exception of a milky-opaque stream colour and yellow organic-looking scum on the pipe steel grating on 30/8/17. At first, PAHs were tested for in the presence of a hydrocarbon slick (such as photograph B). Yet after the first two discharges analysed, total PAH concentrations were low and did not reflect the extent of the sampled discharge, thus TPHs were then tested for to gain an understanding of total hydrocarbon presence/ composition. All are hydrocarbon/ oil based, apart from the milky opaque discharge, shown in the photograph in the bottom middle below (photograph C).

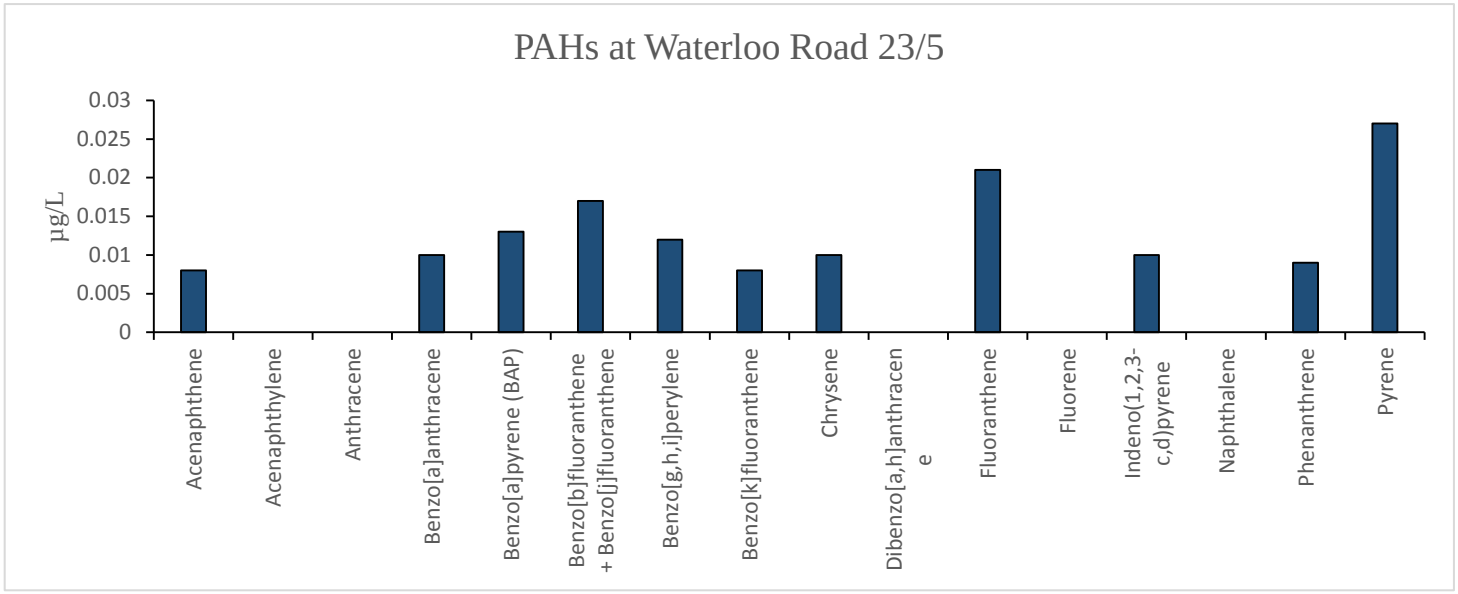
Figure 3.8 Discharges seen at Waterloo Road

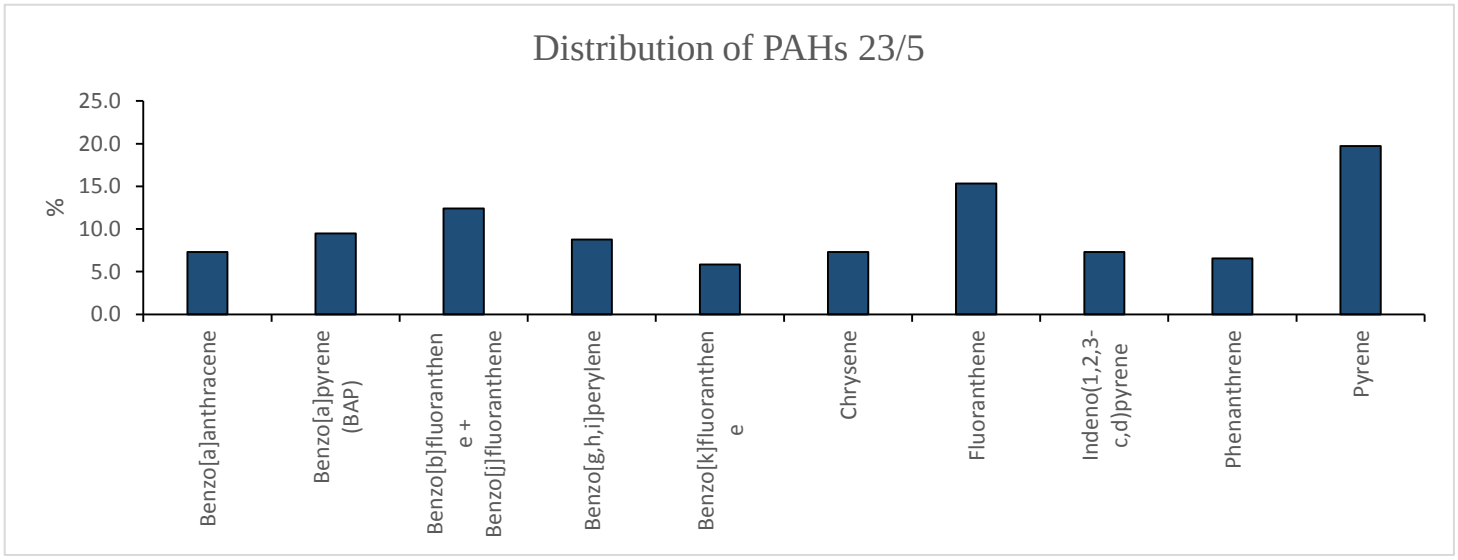
PAHs at Waterloo Road

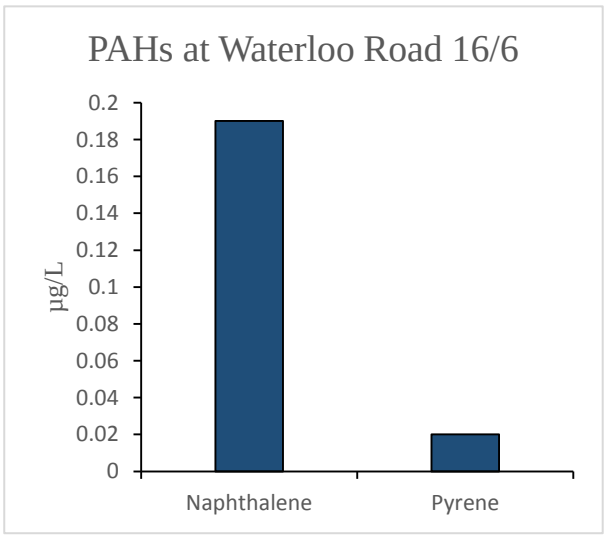
PAH analysis from the first two sampled discharges at Waterloo Road are presented in Table 3.10 and Figure 3.9. In both the samples, low molecular weight PAHs dominated in occurrence, with Pyrene present in both. PAHs overall were at low concentrations in the two sampled discharges at Waterloo Road, with the first discharge having many more present, yet still at low concentrations just above detection limit.

Table 3.10 PAH analysis at Waterloo Road

PAH	WAR discharge 23/5	WAR discharge 16/6
Acenaphthene	<0.008	<0.008
Acenaphthylene	<0.008	<0.008
Anthracene	<0.008	<0.008
Benzo [a] anthracene	**0.01**	<0.008
Benzo [a] pyrene (BAP)	**0.013**	<0.008
Benzo [b] fluoranthene + Benzo [j] fluoranthene	**0.017**	<0.008
Benzo [g,h,i] perylene	**0.012**	<0.008
Benzo [k] fluoranthene	**0.008**	<0.008
Chrysene	**0.01**	<0.008
Dibenzo [a,h] anthracene	<0.008	<0.008
Fluoranthene	**0.021**	<0.008
Fluorene	<0.008	<0.008
Indeno (1,2,3-c,d) pyrene	**0.01**	<0.008
Naphthalene	<0.04	**0.19**
Phenanthrene	**0.009**	<0.008
Pyrene	**0.027**	**0.02**
Sum (∑) PAHs	**0.137**	**0.21**







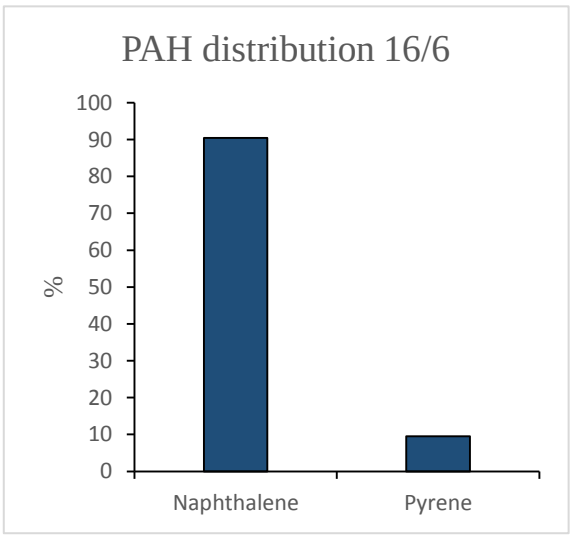


Figure 3.9 PAH concentrations from two discharges at Waterloo Road (from photograph B and 23/5)

TPHs at Waterloo Road

After these results, a TPH test was adopted instead of PAHs for hydrocarbon-looking discharges (such as for photograph E in Figure 3.8). Table 3.11 below displays results of TPH tests in the catchment (results in mg/L). The discharge on 25/7 was predominantly associated with high-C compounds (13.1 mg/L C15-C36), which was also the case for a similar slick seen downstream, indicating the same source.

Table 3.11 TPH concentrations from discharges at Waterloo Road

Discharge location & date	C7-C9	C10-C14	C15-C36	Total TPHs
Waterloo Road 25/7	<0.06	<0.2	13.1	13.1
Gerald Connolly Place 25/7	<0.06	<0.2	2	2
Waterloo Road 18/8	<0.06	<0.2	<0.4	<0.7

On 25/7, a sticky-lubricant looking discharge was observed at WAR (photograph E in Figure 3.8), which appeared to move downstream to GCP (Table 3.11), where there was then another dry-weather pipe discharge into the stream observed. To understand what was being discharged from the pipe, and to determine separate contaminant sources, samples of nutrients were taken from the GCP pipe and stream at WAR for comparison (Figure 3.10). From this, the pipe at GCP appears the source of elevated ammonia, whereas the hydrocarbon slick was sourced around WAR (higher concentrations there) and travelled downstream to GCP.

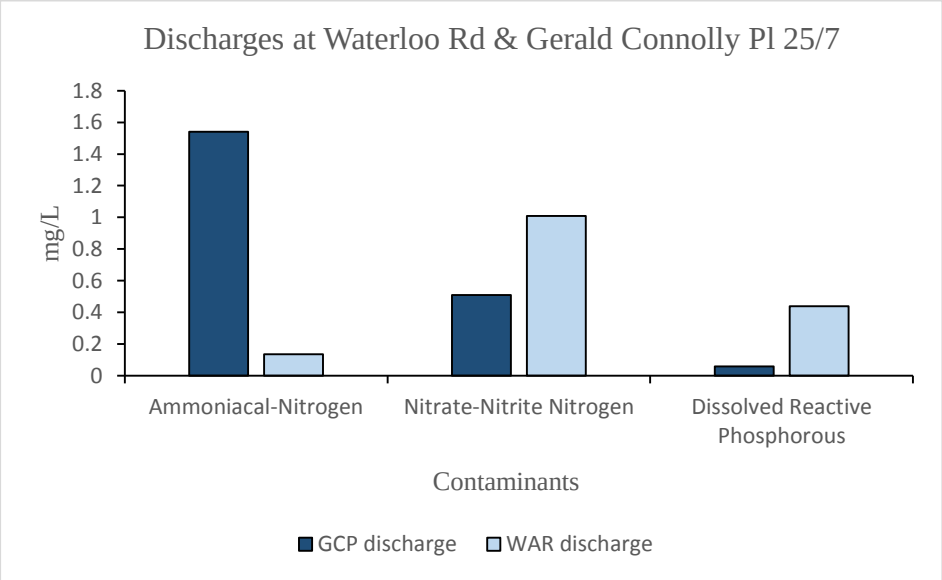


Figure 3.10 Results of sampled discharges at WAR and GCP 25/7/17

Milky stream at Waterloo Road 30/8

On 30/8 the stream at Waterloo Road was an opaque milky-white colour (photograph C in Figure 3.8), where the stream bed was not visible through the water column. As this was a scheduled day for sump sampling, a field kit was present to take physio-chemical measurements, as well as samples for nutrients. The stream had a high pH, low dissolved oxygen and high conductivity (Table 3.12). On the steel grating of the stormwater pipe exit, there was a yellow, fibrous looking scum substance that was also sampled for *E. coli*, as it appeared to be organic in origin.

Table 3.12 Milky-opaque stream on 30/8 discharge results

Discharge	Temp (˚C)	pH	DO (mg/L and % saturation)	Conductivity (µS/cm)	A-N (mg/L)	NNN (mg/L)	DRP (mg/L)	*E. coli* (MPN/100 ml)
Milky stream	10.9	8.85	2.82 (25.8%)	459	0.66	22	0.033	-
Yellow scum	-	-	-	-	-	-	-	>1600

It is clear that that whatever produced this discharge signature was a high-ionic discharge (high conductivity and highly-elevated NNN) and had a possible high organic component to it (high *E. coli* and low dissolved oxygen in the stream- potentially from the organic matter consuming oxygen in the water column). This discharge signature was not seen again during field visits, yet is highly concerning considering the concentrations of instream pollutants (particularly ammoniacal-N and NNN) and stream condition (low DO, high pH and conductivity) seen during a baseflow condition.

Washbournes Road

Haytons Stream re-emerges from the stormwater network at Washbournes Road as a box-drain style waterway, flowing between industrial sites until its confluence with Paparua Stream. There are many stormwater pipes along the side of the stream at this site, three of which were observed discharging in dry weather (Figure 3.11), with two separate pipes sampled (one pipe sampled twice- three samples overall- Figure 3.12).

Figure 3.11 Pipes seen discharging downstream of Washbournes Road

Of these photographs, pipe A was observed discharging on 23/3, 5/5 and 29/5 in dry weather, and was sampled on 5/5 and 29/5 to compare concentrations. The second pipe (B) was caught discharging on 8/9 and was sampled. Pipe C was seen on a sporadic visit where sampling equipment was not available, yet pictures and location were passed on to local authorities.

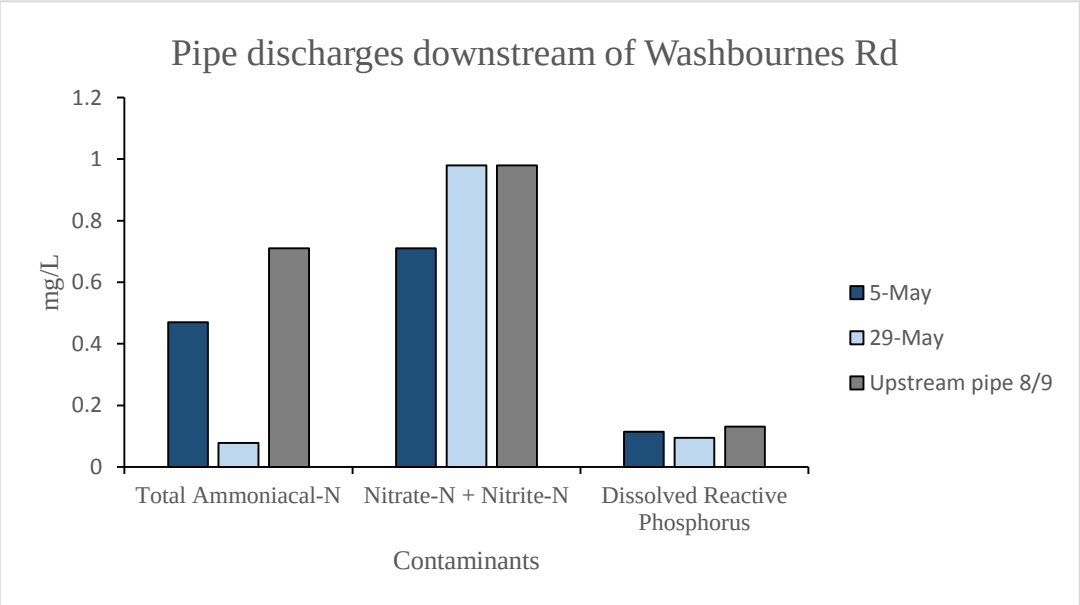


Figure 3.12 Results of pipe discharges downstream of Washbournes Road

Gerald Connolly Place

On 27/9, upstream of the usual sampling point at Gerald Connolly Place, there was a large, shiny (glitter-like) scum on the stream surface that had a strong sewage smell (Figure 3.13). The scum was sampled, and contained low concentrations of nutrients, yet a high *E. coli* concentration of 517 MPN/100 ml (Table 3.9). This high *E .coli* during what was a dry weather (baseflow) condition does appear to suggest a form of sewage or organic material pollution near this site, especially considering the maximum baseflow *E. coli* concentration at WAR (a few hundred metres upstream), was 61 MPN/100 ml over three separate baseflow runs.

Figure 3.13 Sewage smelling scum at Gerald Connolly Place 27/9/17

3.4 Discussion

Physio-chemical parameters

The pH in Haytons Stream was predominantly within the range suggested for the urban streams in Canterbury (Environment Canterbury, 2011). Median pH tended to decrease with rainfall, which has been reported previously in Haytons Stream, as slightly acidic rainfall stripping carbon dioxide from the atmosphere enters the waterway (Moores et al., 2009). The high pH values of 8.57 and 8.54 recorded at WAR and GCP respectively suggest potential pollution sources with rainfall, and require further investigation. Instream temperature was generally higher during stormflow, with stormwater runoff from warmer impervious surfaces likely causing this increase. Temperatures did not change dramatically between dry and wet weather (although samples were collected outside of summer months). Conductivity was variable throughout Haytons Stream and between weather events. At sites WAR and GCP, stormflow tended to reduce instream conductivity, which has been reported previously in this catchment as rainfall is of lower conductivity than the baseflow water column (Moores et al., 2009; O'Sullivan and Charters, 2013). However in the mid catchment, specifically sites WBR, LSA and TRW, average conductivity was higher in stormflow than baseflow, suggesting a source of ions/ nutrients near these sites washes off with rainfall.

The marked depressions in DO far below saturation found in Haytons Stream can indicate a stream receiving waste water, or excessive amounts of nutrients from diffuse pollution (Wilcock, 1986). Haytons Stream has had low DO concentrations reported consistently (Moores et al., 2009; O'Sullivan and Charters, 2013), with this study further supporting this idea. The higher DO concentrations during stormflow have also been reported previously, likely due to instream mixing from runoff generating turbulence and higher oxygen levels (Moores et al., 2009).

Trace elements

Of the contaminants measured throughout the stream, the trace element concentrations are of high concern given the magnitude and frequency of exceedances found across the catchment. The concentrations of numerous parameters and contaminants indicate that the stream has not improved in water quality since its last investigation, particularly for trace elements. Numerous metals exceeded ANZECC species protection guidelines throughout Haytons Stream in this study, yet as the stream is classified as part of the stormwater network, eventually confluencing with the Heathcote River/ Ōpāwaho, the 80% ANZECC guidelines have previously been used for reference in this catchment (O'Sullivan and Charters, 2013). Metals that frequently exceeded this guideline in Haytons Stream included Al, Cu and Zn, with occasional spikes in Cd and Pb in stormflow conditions. Exceedances in these metals are not completely surprising, as they are commonly reported at elevated concentrations

in urban waterways that drain impervious/ urbanised land worldwide (Paul and Meyer, 2001; Walsh et al., 2005), and across New Zealand (Margetts and Marshall, 2016; Milne and Keenan, 2008).

These metals are an issue in Haytons Stream both due to the concentrations found and the magnitude of exceedances compared to relevant guidelines. Zinc, often the most prominent anthropogenic metal in urban environments, was found at levels 40-times the ANZECC 80% guideline in baseflow, and 26-times the guideline during stormflow. As discussed in chapter two, zinc sources are abundant in this industrial catchment, with ubiquitous, aged building materials (such as old galvanised roofing and sidings), heavy truck tyre and break pad use (leading to engine wear) likely providing constant and substantial quantities of zinc to the stream, as has been found in similar urban catchments (Beasley and Kneale, 2002; Davis et al., 2001; Charters, 2017). It is important to note that Haytons Stream emerges from Waterloo Road, a busy industrial road hosting abundant large trucks with stop-start traffic behaviour. This road is likely a major source of zinc and other metal deposition during antecedent dry periods. Roads with over 5000 vehicles per day have been reported to have more polluted runoff than highways, due to stop-start traffic and site specific factors (Huber et al., 2016). Waterloo Road may be of smaller size, yet the constant large-wheeled vehicle traffic will undoubtedly deposit significant concentrations of metals at all times. Importantly, Zn was predominantly present in the dissolved phase, as has been commonly reported, and is of a greater ecological concern being a more bioavailable fraction of metal (Sansalone and Buchberger, 1998). The highly elevated baseflow concentrations of dissolved Zn coupled with the high concentrations of labile Zn found in sediment (in chapter two) support the hypothesis that the bed sediment is a constant source of Zn to the water column, as was proposed in previous research (Moores et al., 2009; O'Sullivan and Charters, 2013; Marshall and Burrell, 2017). It also suggests that a large proportion of Zn may be sourced from areas that generate dissolved zinc phases, such as old painted and unpainted galvanised roofing or building sidings (Charters, 2017; Davis et al., 2001), of which there appears a high density throughout the catchment.

Copper commonly exceeded the 80% ANZECC guideline throughout Haytons Stream, with concentrations generally higher in stormflow, yet Cu still exceeded the 80% guideline at a number of sites throughout Haytons Stream during dry weather. Copper contamination has been related to the density of vehicle usage and flow of vehicles; and as copper is a major component in vehicle brake pads (Davis et al., 2001), dry weather elevations in Cu may be sourced from vehicle usage in this catchment, and have similar transport mechanisms and sources to Haytons Stream as Zn. Similar to Zn, dry weather elevations in Cu also suggest that the bed sediment is a source to the water column. Copper is also sourced from building sidings (Beasley and Kneale, 2002; Davis et al., 2001), and is largely transported via road runoff. The dry and wet weather elevations in copper (with particularly high stormflow concentrations) support previous research that Cu is transported to Haytons Stream at higher concentrations during rainfall, which corroborates with this study's previous chapter, finding elevated Cu throughout the bed sediment of the stream (particularly in the industrial upper catchment directly

draining the stormwater network), as well as with the Pearson correlations suggesting a similar source of Cu and Zn to Haytons Stream.

Cadmium is commonly found in urban environments (Paul and Meyer, 2001), and was elevated at specific sites and conditions throughout Haytons Stream. Stormflow concentrations of Cd reached orders of magnitude higher than guidelines at a number of sites, indicating stormwater runoff is a major transport mechanism for Cd to the stream. Partitioning of Cd was inconsistent with previous reports, where Cd is primarily dissolved (Sansalone and Buchberger, 1998), and was found in high particulate percentages across Haytons Stream, particularly during stormflow. In baseflow, Cd spiked at Washbournes Road consistently, indicating a nearby dry weather source. This also matches the large spike in sediment cadmium concentrations found in chapter two, at identical sampling sites. During stormflow, concentrations were higher across the catchment and indicate mass wash-off occurs across the industrial catchment. Common Cd pollution sources to soil and water include lubricating engine oils, tyre usage, super phosphate fertilisers, electroplating industries and Cd-Ni batteries (Nordberg, 1974; Sutherland, 2000) ; the majority of which are present in the Haytons Stream catchment. It is likely that wash-off from industrial operation carries Cd to the stream during rainfall; often seen through higher concentrations in the upper catchment than the lower pastoral catchment. However, there was a consistent source of Cd downstream of the Wigram Retention Basin, which may be from fertiliser or pesticide/ chemical application in the pastoral farmland area (Cd also predominantly particulate at this site). An individual Cd concentration of 221 µg/L at Waterloo Road during stormflow one indicates point-source industrial pollution, or poor hazardous substance/ stormwater management in the upper catchment.

Pb was elevated throughout Haytons Stream in this study (although predominantly in particulate form), despite the fact lead is seen at reduced concentrations in modern urban environments due to decreases in lead paint and uptake of unleaded fuels (Paul and Meyer, 2001). Even after accounting for legacy effects of lead from the historic uses, Pb can still enter freshwater environments from vehicle brake and tyre wear, emissions from gasoline-powered machinery, lubricating motor oils, rubber and concrete (Beasley and Kneale, 2002; Förstner and Wittmann, 2012; Sutherland, 2000). Elevated lead concentrations in water (particularly during stormflow) indicate that these sources are continuing to pollute Haytons Stream with Pb, however it is predominantly present in particulate-bound phases.

An interesting finding of this study was the elevated concentrations of aluminium during baseflow and particularly stormflow throughout Haytons Stream. Baseflow concentrations were consistently above the 150 µg/L 80% ANZECC guideline (at pH >6.5), with stormflow concentrations magnitudes higher throughout the catchment. A large number of industrial operations from automotive, engineering and construction all use aluminium in their products, with misuse/ mishandling of such products leading to release of Al to the environment (Klöppel et al., 1997). If individual industrial sites leave aluminium

products scattered and un-cared for (such as wires, sheeting, foils and aluminium components of machinery), aluminium could be released from these sites via weathering or through corrosion from industrial exhaust fumes (Klöppel et al., 1997). The large majority (85-99%) of Al in this study was found in particulate form in Haytons Stream, indicating it is not necessarily weathering and stripping of Al ions into solution but particulate-bound metals and potentially whole-metal particulates that are polluting the stream. Aluminium is also the most abundant metallic element in earth's crust, largely associated with alumino-silicate minerals and soil materials, and commonly found associated with particulate matter in aquatic environments (Driscoll et al., 1980; Driscoll and Schecher, 1990). It is likely that there is a combination from the industrial land use, and subsequent volumes of sediment generation and runoff in the catchment that are transporting these elevated concentrations of Al to Haytons Stream.

The concentrations of trace elements in this study suggest that the Wigram Retention Basin does little to remove these contaminants present in Haytons Stream and prevent them from entering the Heathcote River. Most trace element concentrations before and after the basin did not change or decrease appreciably during baseflow conditions (Appendix 4 outlines full concentration data), with some metals increasing in concentration after passing through the basin (Zn, Cu, Cd and Pb all commonly increased through the basin during baseflow). During stormflow, the basin appears to remove metals more successfully, likely due to the increased sediment/ TSS loads during wet weather allowing particulate-bound metals to drop out in the wetland. The Heathcote River downstream of Haytons Stream had significantly higher concentrations of total Al, dissolved Cu and total and dissolved Zn than the upstream site, indicating these metals are of high concern passing through the catchment and polluting the Heathcote's main stem.

When comparing the two different land-uses in the catchment, the industrial upper catchment had significantly higher concentrations of several metals (Al, Cr, Cu, Ni, and Pb), during baseflow and stormflow, indicating that the industrial land use is a source of metals to the stream at all times, during dry and wet weather conditions. There were more dissolved concentrations and partitioning during baseflow, indicating that dissolved metals tend to be in to the stream during dry weather, whereas stormflow and stormwater runoff better facilitates the transport and concentration of particulate-bound metals. This is commonly found worldwide, where urban and especially industrial-urban areas generate higher concentrations of metals, and that non-point sources of metals tend to dominate over point-sources in urban areas (Wilber and Hunter, 1977). Haytons Stream has ubiquitous metal pollution during baseflow, likely due to the extensive array of continual (industrial) metal sources within its catchment, and the contaminated bed sediment that releases metals back into the water column. During rainfall, stormwater runoff facilitates the effective transport of a wide range of metal contaminants to the stream, elevating these concentrations far beyond ANZECC species protection guidelines and far

beyond other Christchurch urban stream reported concentrations, particularly for Zn and Cu (Margetts and Marshall, 2016; Marshall and Burrell, 2017).

Nutrients

Nutrients (specifically DRP and ammoniacal-N) were elevated in the middle catchment at WBR at all times during baseflow. At WBR, DRP was consistently above the 0.01 mg/L ANZECC trigger value for a slightly-disturbed aquatic ecosystem during baseflow, with concentrations reaching 4 mg/L during stormflow. Similarly at the same site, ammoniacal-N was elevated beyond the 0.021 mg/L ANZECC trigger, with stormflow concentrations reaching 13.5 mg/L; far exceeding toxicity values found for New Zealand native fish species common in lowland streams (Richardson, 1997). Williamson (1993) suggested 'high' Event Mean Concentrations in New Zealand urban runoff of 0.07 mg/L DRP and 0.25 mg/L ammoniacal-N, suggesting that the site at Washbournes Road can generate highly nutrient-contaminated urban runoff, far beyond typical urban stormwater concentrations found in New Zealand. Statistically significant differences between Washbournes Road and Waterloo Road/ Upstream of the Wigram Basin (in baseflow and stormflow for DRP) and between WBR and UWB (for baseflow ammoniacal-N) corroborate the significance of the higher nutrient concentrations seen at WBR, despite the low samples sizes (n=3 for baseflow/ stormflow). Concentrations of these contaminants consistently dropped back off again at UWB, indicating the source of nutrients to the stream is close by to the Washbournes Road stormwater network that Haytons Stream re-emerges from.

These findings are consistent with previous investigations along Haytons Stream (particularly for DRP), where Moores et al. (2009) reported elevated concentrations in the mid catchment's stormwater network during dry and wet weather, at similar concentrations. In that study ammoniacal-N was consistently elevated at Gerald Connolly Place, as well as in the middle industrial catchment. Between the time of 2009 and this current study, a known point-source of nutrients (including ammonia) to the stream at Gerald Connolly Place was identified and stopped, yet the high ammonia concentrations at WBR in this study (particularly in stormflow) suggest that the source(s) in the mid catchment is the same and ongoing. This mid-catchment spike in nutrients in the Haytons catchment has been reported over the past 20 years (Brown et al., 1996; Moores et al., 2009; Silveira et al., 2016), with this study verifying its continued presence in the stream. Common sources of nutrients (nitrogen and phosphorous) to urban streams are commonly fertiliser use, wastewater discharge, leaky sewer lines and/ or detergent use (Paul and Meyer, 2001).

The elevated nutrients found at Washbournes Road during baseflow and stormflow in this study were generally not found at the same concentrations downstream in the catchment (at UWB), as the stream flowed through a series of retention pools and denser areas of aquatic vegetation. Recent research has shown that nitrogen transforms along the length of Haytons Stream, from inorganic forms in the industrial upper catchment to particulate organic forms in the lower catchment after the series of deep

retention pools and the Wigram Retention Basin (Silveira et al., 2016). Coupling these findings support the notion that nutrients sourced from the mid catchment are being either taken up by vegetation/ weeds in the lower catchment or transformed into different species, as Haytons Stream flows through the lower pastoral catchment. This study's elevated DRP observations at Washbournes Road corroborate that Haytons Stream has been reported to have higher DRP (up to triple the concentration) than any other Christchurch river site, as well as historically high ammoniacal-nitrogen downstream of the Wigram Retention Basin (Margetts and Marshall, 2016). This again suggests that rainfall wash-off over the impervious surfaces of the catchment (higher DRP during stormflows) are transporting these nutrients to the stream, with a potentially large source nearby the stormwater network that feeds Haytons Stream at Washbournes Road causing this mid catchment spike. This site also had the highest average Haytons Stream conductivity in wet weather in this study, further suggesting that ion/nutrient-laden discharges and/ or stormwater runoff are occurring near this site. It also suggests that instream pollutant concentrations are determined by the individual industrial sites nearby, and not necessarily from weather events or rainfall characteristics. This is shown through large spikes in contaminants at WBR, which are not seen upstream at WAR or downstream at UWB, suggesting that it is not the intensity or duration of rainfall that is determining instream pollution concentrations, but rather the individual industries present and their location which may dictate where (and what) pollution is most prevalent across the catchment.

A large source of nutrients has been previously observed in the Haytons mid catchment, where NIWA conducted a study of the stormwater runoff quality near the Wigram Retention Basin, finding that there were elevated concentrations of nutrients both upstream and downstream of the WRB. Stormwater monitoring at the outlet pipe of the local fertiliser plant in the catchment showed that this location was a large (yet not sole) source of elevated nutrient concentrations in the catchment (Brown et al., 1996). These findings estimated that the factory contributed around 48% of the ammonia, 100% of the DRP and 76% of the total phosphorous found in 1996. It was noted that these values may be subject to sampling and analytical error, as well as the possibility that there is an accumulation of nutrients discharged from the factory in particulate form in drain sediments (Brown et al., 1996). In recent additional research, Silveira et al. (2016) found that the middle-section of Haytons Stream (around Washbournes Road) was consistently elevated in various nitrogen species including Total Nitrogen, Dissolved Organic Nitrogen and ammoniacal-nitrogen, as well as finding a point-source discharge of DON and NH_4-N at this site (Silveira et al., 2016). This study's findings confirm both the research of Brown et al. (1996) and Silveira et al. (2016), presenting substantial and continued evidence that Haytons Stream still receives contaminant-laden discharges across the catchment, and particularly nutrient discharges in the mid catchment.

Nitrate-Nitrite concentrations were higher during baseflow throughout Haytons Stream, consistently in exceedance of the 0.444 mg/L ANZECC trigger value. However, concentrations throughout the stream

are consistent with groundwater in the area, and are comparable to the already-elevated nitrate concentrations found across Canterbury and parts of Christchurch (Hanson, 2002). This also explains why NNN concentrations tend to be lower in stormflow, as the incoming stormwater of lower NNN will dilute the stream baseflow concentration.

Total Suspended Solids (TSS) concentrations were generally below guidelines during baseflow, and were consistently decreased downstream. However, dry weather concentrations still suggested substantial suspended matter in the water column (particularly at WAR), suggesting that the riparian plantings in the upper catchment are doing little to remove industrial particulates from entering the waterway. Stormflow concentrations were commonly much higher, likely due to particulate matter wash-off from industrial surfaces and eventual instream deposition. Similar trends have been reported in previous Haytons Stream monitoring, and at similar concentrations (Moores et al., 2009; O'Sullivan and Charters, 2013).

Stormflow concentrations of *E. coli* commonly exceeded the 550 MPN/100 ml guideline for lowland streams, yet none of the three sampled sites had an exceedance during baseflow. This suggests that *E. coli* is predominantly transported to the stream via rainfall wash-off (i.e. non-point source), which is not surprising given that urban runoff is known to hold high levels of bacteria (Young and Thackston, 1999).

Implications for management from water sampling

From the additional contaminants sampled, it is evident that rainfall is a transport mechanism for contaminants to Haytons Stream, particularly for suspended solids, nutrients and *E. coli*. Suspended solid concentrations could be targeted through upgrades or modifications to existing stormwater infrastructure to trap gross pollutants such as sediments, to reduce the amount of suspended material washed off into the stream during rainfall. Elevated nutrient concentrations are specifically in the middle catchment around Washbournes Road, and thus pollution prevention and stormwater management may be most effective around that area. The elevated concentrations of DRP and ammoniacal-N in the middle catchment have been found previously (Brown et al., 1996; Moores et al., 2009), and suggest that the source(s) of nitrogen and phosphorous to the stream are still present. Specifically, the use/ manufacture of fertilisers, chemicals and industrial cleaning products containing nitrogen and phosphorous compounds should be addressed and further audited to mitigate their potential presence, storage or misuse within or near the stormwater network which eventually feeds into Haytons Stream.

Reactive discharges sampled

Of the twelve separate situations where evidence of dry weather discharges were observed in the catchment, six of these occurred at the first site on Haytons Stream, at Waterloo Road. Three samples were taken at Washbournes Road (two of which were from the same pipe), and two were taken at Gerald

Connolly Place. This suggests that there is a higher frequency of dry weather discharges to the stream in the upper catchment, where most are seemingly discharged via the stormwater network, above where there is open channel stream flow. Almost all discharge signatures at Waterloo Road were hydrocarbon-based, indicating dry weather discharges into the stormwater network are a predominant issue for upper catchment businesses. It has been suggested that the majority of hydrocarbon inputs into storm drains (both accidental and intentional) could be from crankcase oil, and particularly heavy lubricant oils (Hunter et al., 1979). A TPH sample in this study returned a high C-range composition in the sample, exiting the Waterloo Road stormwater network. Close comparisons have been made between the chemical compositions of hydrocarbons used in automobile oils, and those found in urban stormwater runoff (Hoffman et al., 1982; Wakeham, 1977). These engine oils typically return TPH chromatograms with high ratios of higher C-ranges (Gustafson et al., 1997). Hydrocarbons and large C-containing compounds such as lubricants and oils are commonly used in automotive (or similar) industries, of which there are abundant businesses in the upper Haytons catchment whose nature of operations would frequently use such products. High occurrences of automotive industries inappropriately connected to storm drain systems have been previously reported, and high percentages of these industries have previously been found to discharge to their local stormwater system (Schmidt and Spencer, 1986). As oil disposal/ pollution is likely at an individual level, pollution prevention programmes and action/ education may be justified to focus on such industries that use or generate oil or hydrocarbon wastes (Whipple and Hunter, 1979), to avoid discharge to nearby waterways.

Of the two PAH samples taken at Waterloo Road in this study, there was a mixture of high molecular and low molecular weight PAHs in the first sample, and only two PAHs (both LMW) present in the second. This suggests that there was a mixture of pyrogenic (combustion-derived) and petrogenic sources in the first sample, whereas the second was likely petrogenic derived (Brown and Peake, 2006). However, only one grab sample of each was taken, and detected PAHs were at low concentrations, meaning potential for fingerprinting was limited. PAH fingerprinting is often conducted using sediment samples (due to where the molecules preferentially bind) (Brown and Peake, 2006), and therefore future desired PAH fingerprinting should use sediment samples taken from Haytons Stream. The presence of sticky hydrocarbon slicks on the stream surface corroborate the fingerprinting attempt, in that the source(s) are likely from engine oil/ fuel disposal and not solely exhaust fume/ combustion derived.

One discharge signature at Waterloo Road was a milky-white/ opaque stream colour, which has been previously reported in Haytons Stream (O'Sullivan and Charters, 2013). This discharge had a high stream conductivity and pH, low dissolved oxygen, elevated ammoniacal-N and highly elevated NNN concentration. A yellow-looking fibrous scum scattered across the steel grating of the exiting stormwater pipe (on the same day) also returned a very elevated *E. coli* concentration. These high bacteriological and nutrient contaminants found on the day suggest that this discharge may have been from an organic or faecal source, and/ or from a source using excessive industrial chemicals or cleaners,

discharging both pathogenic and chemical contaminant pollution into the stormwater network and Haytons Stream (Field, 1994).

Discharges at Washbournes Road were not hydrocarbon-based, and originated from stormwater pipes discharging straight into the stream in dry weather. These discharges were typically clear to slightly opaque, and occasionally produced a slight foam/ soap after contact with the water column. The concentrations of nutrients from these discharges were typically elevated above ANZECC trigger values. Ammoniacal-N was typically the contaminant of highest concentration, indicating some form of industrial (potentially sanitary or laundry) washwater or wastewater source (Field, 1994), as waste and washwaters from commercial or industrial areas typically have elevated ammonia/ phosphorous and other pollutant concentrations (Field and Pitt, 1990; Lalor, 1993; Pitt, 1993). Nutrient concentrations sampled from the pipe discharges at Washbournes Road rule out spring or tap water sources, and generally point to some form of industrial process-water discharge, the typical/ expected concentrations of which have been stated and verified through multiple field investigations elsewhere (Field, 1994).

Of the two discharges captured at Gerald Connolly Place, the pipe discharge was a source of elevated ammoniacal-N to the stream, yet contained low concentrations of other contaminants. This high ammonia content directly leaving an adjacent businesses site was likely from industrial washwater (Field, 1994), and was passed on to relevant council employees who were able to make contact and cease future occurrences from the pipe. The glitter-looking brown scum on the stream surface at Gerald Connolly Place remains unsolved. The elevated *E. coli* beyond recorded baseflow concentrations suggests clear bacteriological (and potentially sewage) pollution, yet the discharge could not be traced or found further upstream from its location, limiting the ability to trace back to a particular industry or pipe. Misconnections leading to bacteriological contamination are common in residential, commercial and industrial areas (Ellis and Butler, 2015; Revitt and Ellis, 2016), however this event may be more of a one-off inappropriate discharge, as it was not seen again during any other field visit.

3.5 Conclusions

Concentrations of contaminants measured in this study were similar to those reported previously in Haytons Stream, indicating that the stream has not improved in water quality during the eight years since these contaminants were last investigated. Generally, contaminant concentrations were higher in wet weather (particularly for nutrients), although elevated concentrations of metals were found throughout the stream during baseflow conditions. Metal pollution is persistent throughout the catchment, with many sampling sites exceeding the ANZECC 80% guideline for metals, with significantly higher concentrations appearing in the upper catchment, indicating the industrial land use and subsequent activities are major sources of metal pollution to the stream. Chapter Two and three of this thesis corroborate that the bed sediment of Haytons Stream is also likely a source of metals back to water column, creating the high dissolved fractions (particularly Zn) seen during baseflow. The mid-catchment site of Washbournes Road had significantly higher concentrations of DRP and ammoniacal-N, which reached highly elevated concentrations during stormflow. These concentrations were not found in the upper catchment (WAR) and generally dropped off/ diluted towards the lower catchment (UWB), indicating that there is a specific source of these nutrients to the stream in the mid catchment, with stormwater runoff via rainfall the main transportation mechanism conveying these contaminants to the stream itself (although concentrations were still commonly above trigger values during baseflow).

Dry weather discharge signatures were observed throughout the catchment, yet were mainly at the first point of open-channel flow, exiting the stormwater network on Waterloo Road. These were predominantly associated with hydrocarbon slicks or odours, suggesting automotive (or similar) industries need to be continually targeted and audited in the upper catchment for industry-specific pollution prevention, to avoid future discharges to Haytons Stream. Dry weather pipe discharges around Washbournes Road tended to contain elevated ammoniacal-N over any other contaminant, suggesting industrial process waste or washwater was predominantly discharged into the stormwater network near this location.

Chapter 4 Identifying potential point-source discharges and stormwater sump contamination in the Haytons Stream catchment

4.1 Introduction

When assessing the extent and sources of contamination in an urban waterway, it is important to consider the wide variety of pollution sources available. In highly impervious catchments, non-point source runoff and untreated stormwater discharge are large contributors to urban stream pollution. Additionally, illicit point-source/ dry-weather discharges can contribute large percentages of annual pollutant loads to a catchment, within one or few concentrated plumes (Field, 1994; Pitt, 1993). Identification of illicit dry weather discharges have been primarily focussed on field presence, mapping and use of tracers for the identification and sampling of discharge outfalls (Field et al., 1994). In New Zealand, the Resource Management Act 1991 Section 15 (1) states that no person may discharge a contaminant into water or onto land unless it is expressly allowed by a regional rule or resource consent. The Canterbury Natural Resources Regional Plan (replaced by the Land and Water Regional Plan) prevents the discharge of certain contaminants to surface water, in the interests of avoiding significant adverse effects to water quality and aquatic ecosystems (Environment Canterbury, 2011).

The previous chapters have discussed the concentrations of contaminants found within the bed sediment and water column of Haytons Stream, providing evidence and discussion of their potential sources in the catchment. However, additional contaminant sources may exist (e.g. from illicit discharge and inappropriate use of the stormwater network) and require investigation and cessation for long-term water quality in Haytons Stream to improve. Moores et al. (2009) reported that Haytons Stream was receiving point-source discharges during dry weather, with observations from continuous data sondes recording water level, conductivity, turbidity and ammoniacal-nitrogen fluctuations in dry weather, independent of rainfall. This investigation also found that contamination of ammoniacal-N can occur in both dry and wet weather, corroborating the findings of Brown et al. (1996), and highlighting that nutrient pollution and illicit use of the stormwater system was still ongoing.

These occurrences were further found by O'Sullivan and Charters (2013), who again found the incidence of regular baseflow fluctuations in Haytons Stream water level via continuous logging (at Gerald Connolly Place). This logging was at a different location on Haytons Stream than that of Moores et al. (2009), and indicated that the stream was receiving discharges in dry weather (i.e. fluctuations in baseflow water level) four years after the original investigation, albeit at a different location. O'Sullivan and Charters (2013) also documented the occurrence of a visible stormwater pipe discharge to the stream during dry weather, and a total of four different discharge signatures observed during baseflow conditions, being; opaque-white, turbid and odorous, petroleum/ hydrocarbon oily sheen, and surface

scum with lather foam (O'Sullivan and Charters, 2013). The upstream open-channel section of the stream was walked numerous times under these conditions to locate a point-source of the discharges, which on all but one occasion, originated from the reticulated stormwater network above Waterloo Road (O'Sullivan and Charters, 2013).

The Haytons Stream catchment also has an abundance of industrial stormwater sumps, draining individual business sites. Sumps (catch basins/ gully pots) have been shown to hold significant quantities of pollutants both before and after storm events, with research showing that the materials held inside sumps can exceed environmental guidelines in their own right, having the potential to adversely impact downstream aquatic environments when that water is flushed out (Brown and Peake, 2006; Pitt, 1985; Stone and Marsalek, 1996).

Much like urban waterways, the types of pollutants found in sumps will vary according to land use. Studies have shown that the chemical quality of sump sediment is similar to that of the street surfaces which they drain (Pitt, 1985), indicating that the pollutants that build up on a given urban surface are likely to end and reside in the sump for a period of time, before being flushed out of the system. It is of interest for pollution prevention measures, and for greater understanding of contaminant discharges in the Haytons catchment, to characterise the quality of supernatant water within industrial sumps, before their eventual discharge to the stormwater network and Haytons Stream. Increased knowledge and quantification of contaminants present in selected (and potentially contaminated) sumps may allow more effective management and action to reduce the discharge of harmful pollutants to Haytons Stream. Quantification of contaminants in industrial sumps will also allow further targeted pollution prevention and hazardous substance education in the catchment, to mitigate future inappropriate disposals to the stormwater system. Therefore, a one-off sampling campaign was conducted across a number of industrial site stormwater sumps, in order to create a snapshot of contamination potential from potentially-polluting industries in the Haytons catchment.

The aims of this chapter are two-fold, yet amalgamate to create an increased understanding of the potential pollution of Haytons Stream via the subsurface drainage system. Past investigations have highlighted the use, practicality and relatively cheap method of continuous logging to identify dry-weather discharges to a waterway. This chapter presents result from the first aim of the use of continuous data loggers to identify dry-weather industrial discharges within the catchment, as well as the second aim of analysing supernatant water from industrial site sumps, to assess their potential contamination and contribution to the pollution of Haytons Stream via the stormwater network.

4.2 Methods

4.2.1 Continuous logging

4.2.1.1 Locations, set-up and calibration

Five Odyssey© water level loggers and conductivity loggers were purchased and placed throughout the Haytons Stream catchment (locations and descriptions in Figure 2.1 and Table 2.1) to continuously log these parameters over time, and compare the results to local rainfall data.

The capacitance water level loggers were calibrated prior to installation via a linear logging technique, where two set distances along the length of the logger were noted (e.g. 10 cm and 100 cm), where the values the logger recorded at these levels when immersed into water were noted. This was then saved into the logger's computer to correct back to vertical mm water level fluctuation when in-situ. Water level loggers were set to a resolution of 1 mm and a recording time of every 10 minutes. Conductivity loggers were pre-calibrated and had a resolution of 7 µs/cm and were set to record every 10 minutes. It was later found that these loggers did not accurately record instream conductivity values when compared to a field meter, and that their values were not accurate as the loggers could not record at such low (freshwater) conductivities. However (and more importantly), the trends and fluctuations of instream conductivity could still be picked up and reported, independent of the values or concentrations the logger recorded. This was verified through field (using a conductivity meter) and lab tests (via spiking solutions with higher conductivity) to ensure that the loggers would still report a rise in conductivity when that was the case.

Locations

Logging locations were chosen to target areas of particular interest in the catchment, as well as to log along the length of Haytons Stream. Two loggers were placed down manholes in the upper and middle catchment, placed near industries thought to be risky or of interest for discharges, with the remaining three logger sets installed across the stream at specific points of interest. Loggers were coupled together (one water level and one conductivity at each site), where either a steel fence post was driven into the stream bed with cable-tied PVC pipes holding the loggers upright, or PVC structures created to hold the loggers in place over the middle of the manhole pipes.

Manhole on Waterloo Road

The first loggers in the catchment were placed down a network manhole on Waterloo Road (-43.538192, 172.533743). Loggers were upheld and supported by PVC pipe structures (Figure 4.1) within the pipe infrastructure, allowing the loggers to record in the middle of the manhole, as well as an easy access to the logger's data ports without the need to enter the manhole.

Figure 4.1 Manhole on Waterloo Road with loggers upheld with PVC structures

Haytons Stream at Waterloo Road (WAR)

This logger set (Figure 4.2) was installed at the first point of open-channel flow on Haytons Stream (-43.537606, 172.541844), to log whatever is immediately exiting the stormwater drainage system from the upper catchment.

Figure 4.2 Logger set at Haytons Stream on Waterloo Road

Springs Road/ Versatile car park manhole

These loggers were placed down a large stormwater pipe (A) located in the Versatile car park off Springs Road (-43.544191, 172.545827). Photograph B shows inside the infrastructure (Figure 4.3).

Figure 4.3 Springs Road manhole and view of loggers inside

Haytons Stream downstream of Washbournes Road (WBR)

The third logger set was placed downstream of the sampling site at Washbournes Road (-43.543984, 172.554321), and below a stormwater pipe that was found discharging during dry weather several times during site visits (WBR pipe discussed in chapter three) (Figure 4.4).

Figure 4.4 Logger set downstream of Washbournes Road

Stormwater pool above Wigram Road

The fifth set of loggers were placed in a stormwater 'pool' area immediately upstream of Wigram Road (-43.552845, 172.567658), which were logging immediately below a large stormwater pipe draining new industrial sections in Wigram (Figure 4.5).

Figure 4.5 Logger set downstream of stormwater pipe above Wigram Road

After seven weeks of logging water level (28/4 – 16/6) and three weeks logging conductivity (19/5 – 9/6) it was concluded that the logger location by Wigram Road was not collecting insightful data to determine the occurrence of any dry weather/ point-source discharges at this location (see results section). The logger set was subsequently moved to Haytons Stream at Gerald Connolly Place (-43.540274, 172.543021) to facilitate more intensive monitoring in the industrial upper catchment, and generate comparable data with O'Sullivan and Charters' (2013) continuous logging at this location.

Haytons Stream at Gerald Connolly Place

Loggers were installed at Gerald Connolly Place on 16/6/17, which were placed immediately after the exit of the stream from an underground culvert at the end of the cul-de-sac on Gerald Connolly Place (Figure 4.6).

Figure 4.6 Loggers at Gerald Connolly Place

4.2.1.2 Data collection and interpretation

The loggers were left for a period of 1-2 weeks before the sites were visited and data downloaded onto Odyssey© software, saved, and then loggers re-started. During weekly site visits, loggers were checked to ensure the structural integrity of their support structures, with desiccant sachets inside the logger body replaced, to ensure minimal water was entering the logger case and reaching the battery. Logger data was collected by downloading the Comma Separated Value (CSV) files from the Odyssey© software, which were then interpreted and plotted into Microsoft excel spreadsheets.

Meteorological data

Rainfall data was collected from the same location and climate station as in chapter three, being NIWA's online National Climate Database (CliFlo), where weekly rainfall data was downloaded for the logging periods when made available. As all five logger sets were within the same small catchment, the same rainfall data was used when interpreting each logger. Logger data was interpreted in conjunction with rainfall, using the same methodology in Moores et al. (2009) and O'Sullivan and Charters (2013). This was that when logger water level fluctuated during periods of no rainfall in the catchment (i.e.

fluctuating water level during baseflow), then these fluctuations may be indicative of some form of discharge to the stream/ infrastructure from nearby industry.

4.2.2 Sump sampling

4.2.2.1 Locations

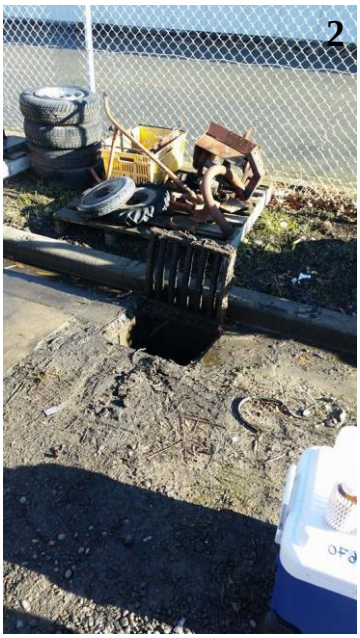
The locations of the nine sampled sumps in the Haytons Stream catchment is presented in Figure 4.7, and each sump is described below (Table 4.1). Potential sampling locations were agreed and planned in conjunction with Environment Canterbury and Christchurch City Council staff, utilising their knowledge of industry and historical pollution in the catchment to create a list of sites that were viewed as 'risky' for contamination, or having potential to contribute pollutants to Haytons Stream via the stormwater network. Sumps were photographed when sampled (Figure 4.8).

Table 4.1 Sump numbers and character in the Haytons Stream catchment

Sump number	Industry character
1	Animal material processing
2	Hydraulic servicing
3	Sanitary equipment cleaning
4	Truck parts/repairs
5	Excavator/van depot
6	Bus repairs
7	Machinery repairs
8	Chemical manufacturing
9	Panel beating/car repairs

Figure 4.7 Sump locations in Haytons catchment (stream in blue) Edited from Google Maps (2017)


1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4


5


6

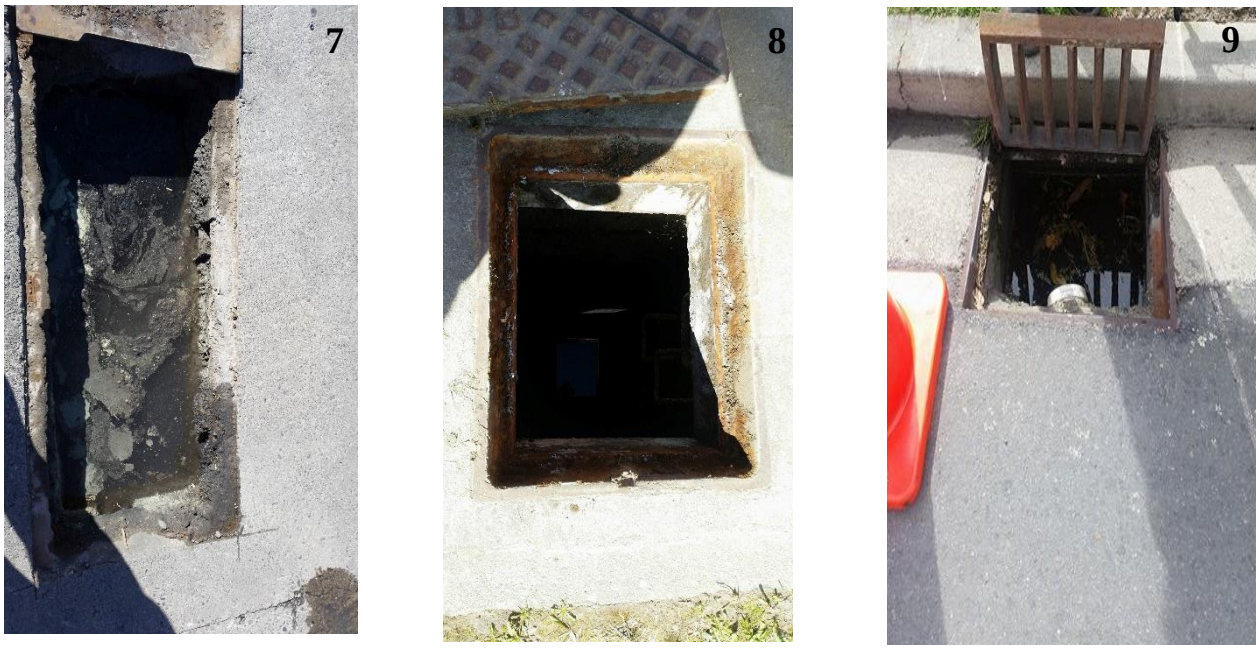


Figure 4.8 Appearance of sampled sumps on the given day (sump numbers displayed). Refer to Table 4.1 for site description

4.2.2.2 Sample Collection

A pre-determined list of stormwater sumps were visited with Environment Canterbury and Christchurch City Council staff in July, September and October to assess their state and overall cleanliness at that time. If a visited sump was in a poor or dirty state that suggested contamination or industrial pollution from poor stormwater/ chemical management, the sump was then sampled. An overall number of nine sumps were sampled to ensure budgeting was spread over the research, whilst still achieving a sufficient spread and number of sump locations. Sampling was undertaken with a minimum of 3 prior dry days, to ensure the sump sampled was not full of 'fresh' rainwater.

Parameters

Chosen sumps with sufficient overlying water were sampled for physio-chemical data (pH, DO, conductivity, temperature) as well as suspended solid, trace element, nutrient, hydrocarbon, organic contaminant and microbiological content in the sump. To ensure consistency in data analysis, all sumps were sampled for the same parameter list, regardless of the nature of industry (Table 4.2).

Table 4.2 Laboratory parameters analysed in sumps

Parameter		Acronym	Units	Analytical method
Trace elements		M	µg/L	APHA 3125B/3030E (for total)
Sediments	Total Suspended Solids	TSS	mg/L	APHA 2540 D
Nutrients	Ammoniacal-Nitrogen	NH_4-N	mg/L	APHA 4500-NH_3 F
	Total Kjeldahl Nitrogen	TKN	mg/L	APHA 4500-N_{org} D
	Nitrate-Nitrite Nitrogen	NNN	mg/L	APHA 4500-NO_3^- I
	Total Phosphorous	TP	mg/L	APHA 4500-P B & E
	Dissolved Reactive Phosphorous	DRP	mg/L	APHA 4500-P E
Microorganisms	*Escherichia coli*	*E. coli*	MPN/100 ml	APHA 9223 B
	Total & Faecal coliforms	TC & FC	MPN/100 ml	APHA 9222 D & 9223 B
Organic contaminants	Chemical Oxygen Demand	COD	g O_2/m^3	APHA 5220 D
	Total Petroleum Hydrocarbons	TPHs	mg/L	US EPA 8015B
	Volatile Organic Compounds	VOCs	mg/L	Headspace, GC-MS SIM analysis

The increased list of contaminants tested in stormwater sumps was a reflection of the wide variety of industries present in the catchment, and what contaminants may eventually be discharged to Haytons Stream. The nutrient suite was widened to include Total Kjeldahl Nitrogen (from which Total Nitrogen can be calculated with NNN), as well as Total Phosphorous. The microbiological parameters of total and faecal coliforms were added to the pre-existing *E. coli* test, to account for organic material industries present in the catchment, as well as TPHs and VOCs due to the nature of many other industries in the catchment. Due to the input of organic and inorganic substances to stormwater sumps, COD is also a useful and commonly adopted technique to assess the amount of oxygen required for the oxidation of organic substances present in a given sample (Butler et al., 1995; Memon and Butler, 2002, 2002).

4.2.2.3 Sample analysis

Physio-chemical data was collected in-situ or from a collection vessel of sample using a HACH 40QD field meter, whilst the other parameters required laboratory analysis. Trace elements and TSS were sampled using the same procedure as in chapter three, analysed at the University of Canterbury. Due to initial preservation errors, dissolved fractions of metals could not be analysed, and therefore only total metal content is reported. All remaining parameters were sampled using appropriate Hill Laboratories sample bottles and submitted to the analytical lab for analysis, using the analytical methods listed in Table 4.2.

4.2.2.4 Quality Assurance/ Quality Control

Samples for UC analysis were duplicated both in the field and in the lab, with the inclusion of method blanks in the analytical process for determining metal concentrations and providing a check for clean and consistent lab work (Table 4.3), such as those discussed in chapter three. All duplicates were under 10% difference, except one for one duplicate where Mo was 14% different. ICP-MS internal standards were used (SRM 1643f) to check for instrument performance.

Table 4.3 Total metal QA/QC data for sump analysis

Element	Detection limit (µg/L)	Blank (µg/L)	SRM 1643f recovery %
Mg	0.1	4.00	84
Al	0.1	49.0	99
Ca	0.1	154	91
Ti	1	0.00	-
V	10	7.30	96
Cr	0.1	0.16	95
Mn	0.1	0.15	93
Fe	0.1	45.8	99
Co	0.1	0.11	91
Ni	0.1	0.00	91
Cu	0.1	1.50	89
Zn	1.0	3.84	93
As	0.1	0.27	100
Mo	1	0.52	101
Cd	0.1	0.01	101
Sb	0.1	0.75	106
Pb	0.1	0.14	93

4.2.2.5 Data interpretation

As all sumps were sampled once, intending to create an initial characterisation/ snapshot of potential contamination and sump water quality, there were limited data analysis options available. Contaminant concentrations in sumps were compared to determine the severity of contamination in relation to other industries across the catchment. Although there are no 'guidelines' for the quality of sump water, this water will eventually be joining the stormwater network before being dispensed into the nearest surface waterway (i.e. Haytons Stream), therefore (not accounting dilution factors and mixing zones) ANZECC guidelines were considered where possible as a rough estimate of sump contamination and polluting-potential. As a crude estimate for high concentrations, the Christchurch City Council's Trade Waste Bylaw guidelines were used (Christchurch City Council, 2015), with the interpretation that if these guidelines were exceeded, the sump is too contaminated to be entering the stormwater network.

During creation of graphs using water level, conductivity and rainfall data plotted against logger dates and times, some graphs had to be shortened and modified in size to fit this document. As a result, for some locations this skews the date and time of rainfall versus water level fluctuation, appearing as if they occur a day or so after the rainfall event. Generally, this is a small and highly impervious catchment, with runoff quickly transferred from the industrial land to the nearest point of Haytons Stream via the piped stormwater network. Thus, large differences between rainfall in the catchment and observed instream water level spikes are the result of shortening and modification of the final plotted data, and not necessarily from actual catchment characteristics.

4.3 Results

4.3.1 Logger data

4.3.1.1 Waterloo Road manhole

The manhole on Waterloo Road was monitored from 28/4/17 to 23/8/17 for water level and from 19/5/17 to 23/8/17 for conductivity. This manhole was downstream of the stormwater network from a number of industries of interest, which eventually led to Haytons Stream via Waterloo Road. This manhole was of interest as a large industry supposedly backwash their filters at regular intervals with clean groundwater, which eventually ends up in this stormwater network (D. Veale, personal communication, February 2017).

Water level

This logger accurately recorded the supposed filter washing at very regular intervals, as well as larger rainfall events which significantly increased the water level within the piped infrastructure (Figure 4.9). The logger occasionally reported negative water level values, which was interpreted as being no or very little flow through the stormwater pipes. The water level loggers worked through capacitance and linear interpretation, therefore if there was very little to no flow for the logger to pick up, the logger likely extrapolated that reading back as a negative value. Appendix 5 presents further data from this manhole (and all other logged locations) at a greater temporal resolution, showing data over one or two week periods to further illustrate the behaviours of water level and conductivity at each location in the catchment.

Conductivity

Conductivity fluctuated over the logging period, with inputs of rainfall through the network tending to spike conductivity, as well as regular inputs via the filter backwashes creating spikes of conductivity at much lower magnitudes, which quickly dropped off again (Figure 4.10). Although the values of conductivity cannot be reported with confidence due to logger capabilities, conductivity remained low and the fluctuations caused by regular filter backwashing did not seem to spike or alter the conductivity trend drastically.

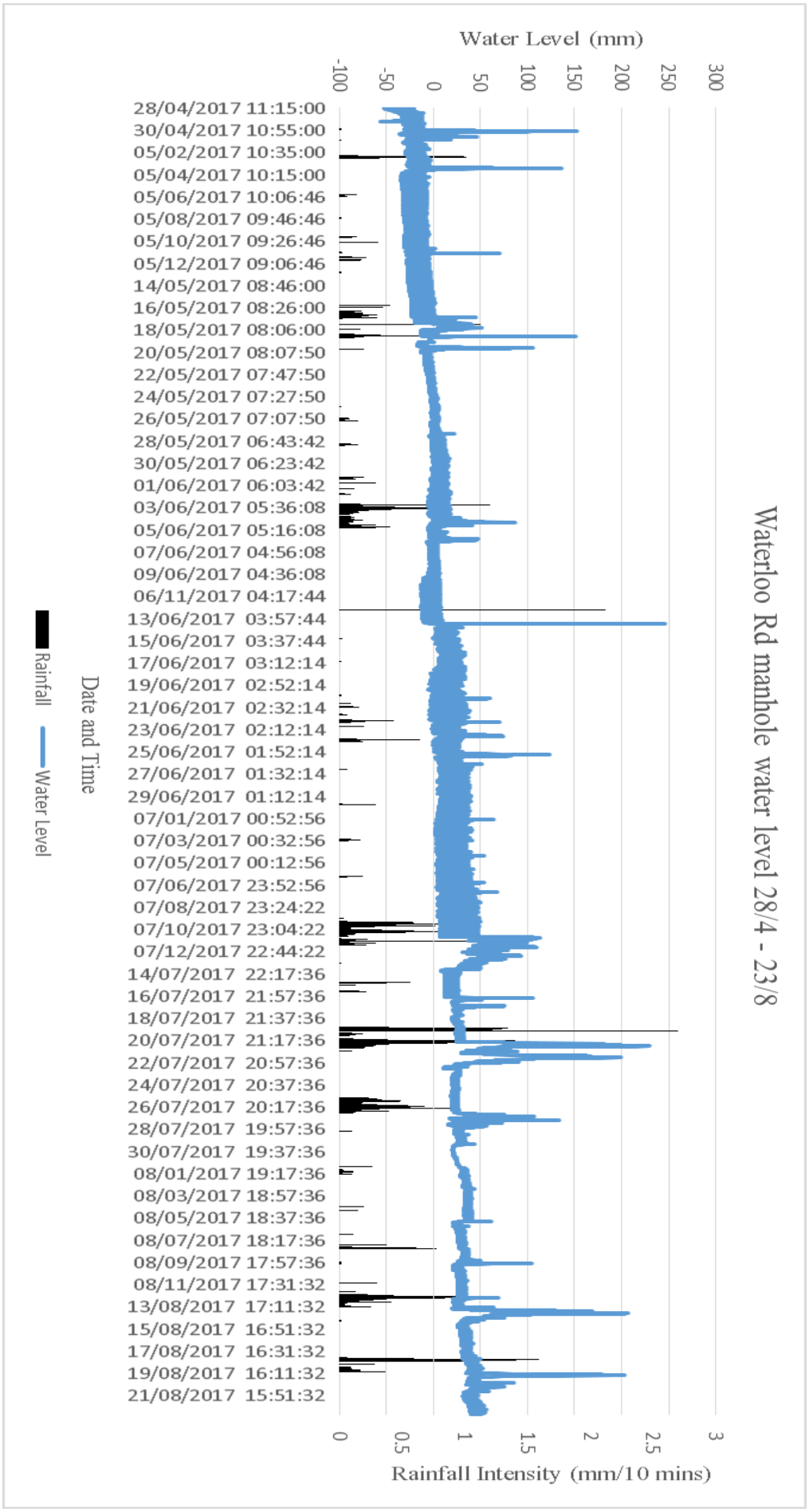


Figure 4.9 Water level in the Waterloo Road manhole

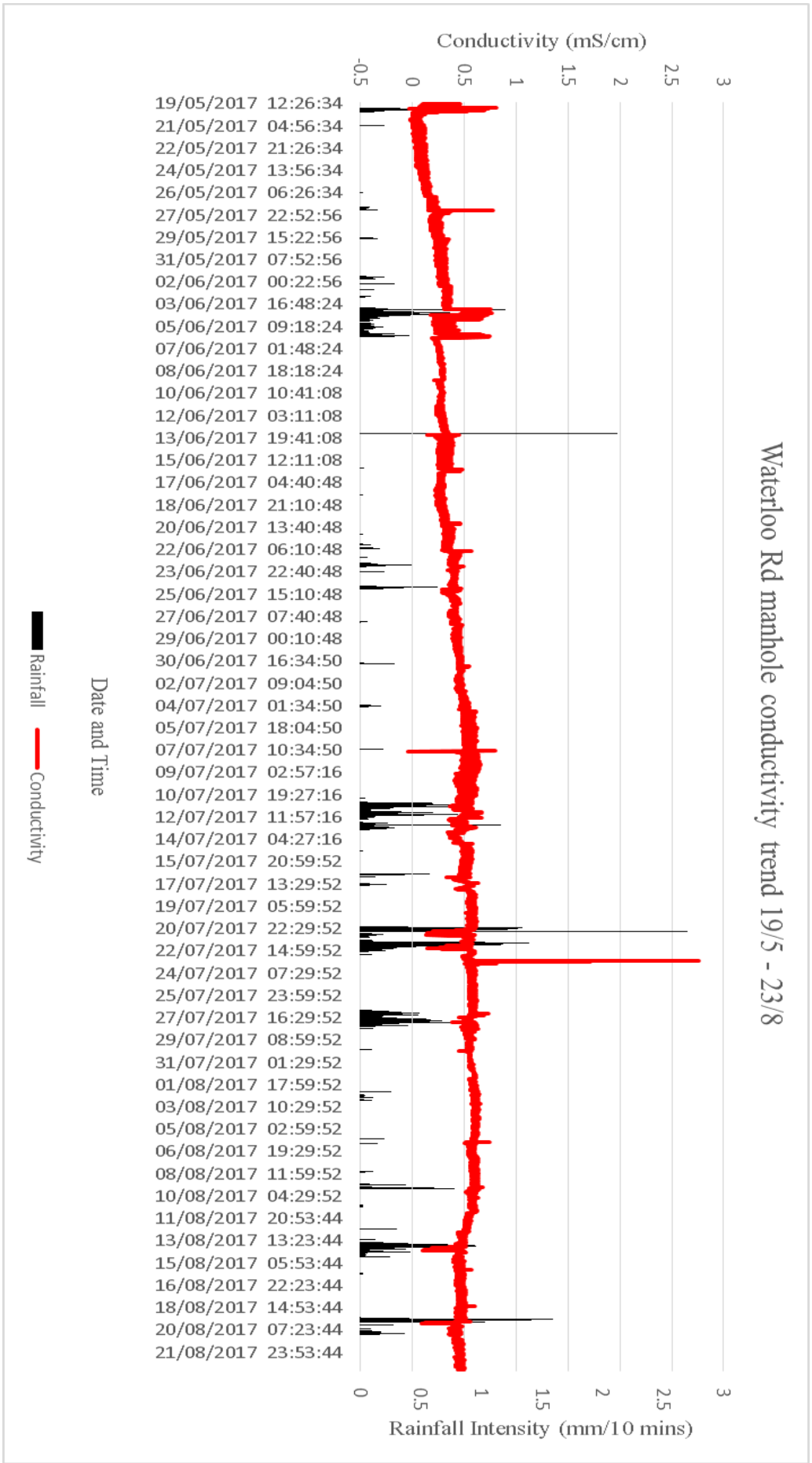


Figure 4.10 Conductivity trend in the Waterloo Road manhole

4.3.1.2 Haytons Stream at Waterloo Road

This logger, placed at the beginning of Haytons Stream emerging from the stormwater network, was logged for water level from 28/4/17 to 23/8/17 (Figure 4.11) and from 26/5/17 to 23/8/17 for conductivity.

Water level

This logger presented perhaps the most interesting and revealing data in the catchment, as it highlights clearly what has been described by Moores et al. (2009) and O'Sullivan and Charters (2013), being the fluctuation of stream water level independent of any rainfall in the catchment (Figure 4.11). As rainfall occurs in the catchment (displayed in mm intensity every 10 minutes), there are larger stream water level peaks that correspond to these additional inputs via runoff into the stream. However, at this location there were also very regular fluctuations (at an almost daily recurrence) of a much smaller magnitude (~50-100 mm) occurring without any rainfall present in the catchment. Appendix 5 contains further data logger graphs (with a higher temporal resolution) from the Waterloo Road site, showing how the stream water level regularly fluctuates both with and without rainfall.

Conductivity

Despite conductivity not recording accurate freshwater values in this location, the trends recorded are of interest. Conductivity remained steady and flat at this location, with only large rainfall/ storm events tending to change the instream trend (Figure 4.12). Despite the regular dry weather fluctuations recorded at this location, the conductivity did not markedly increase during these events. This indicates that whatever is being discharged to Haytons Stream at this location does not alter the instream conductivity severely, and therefore likely represents a solution with low ion/ nutrient content.

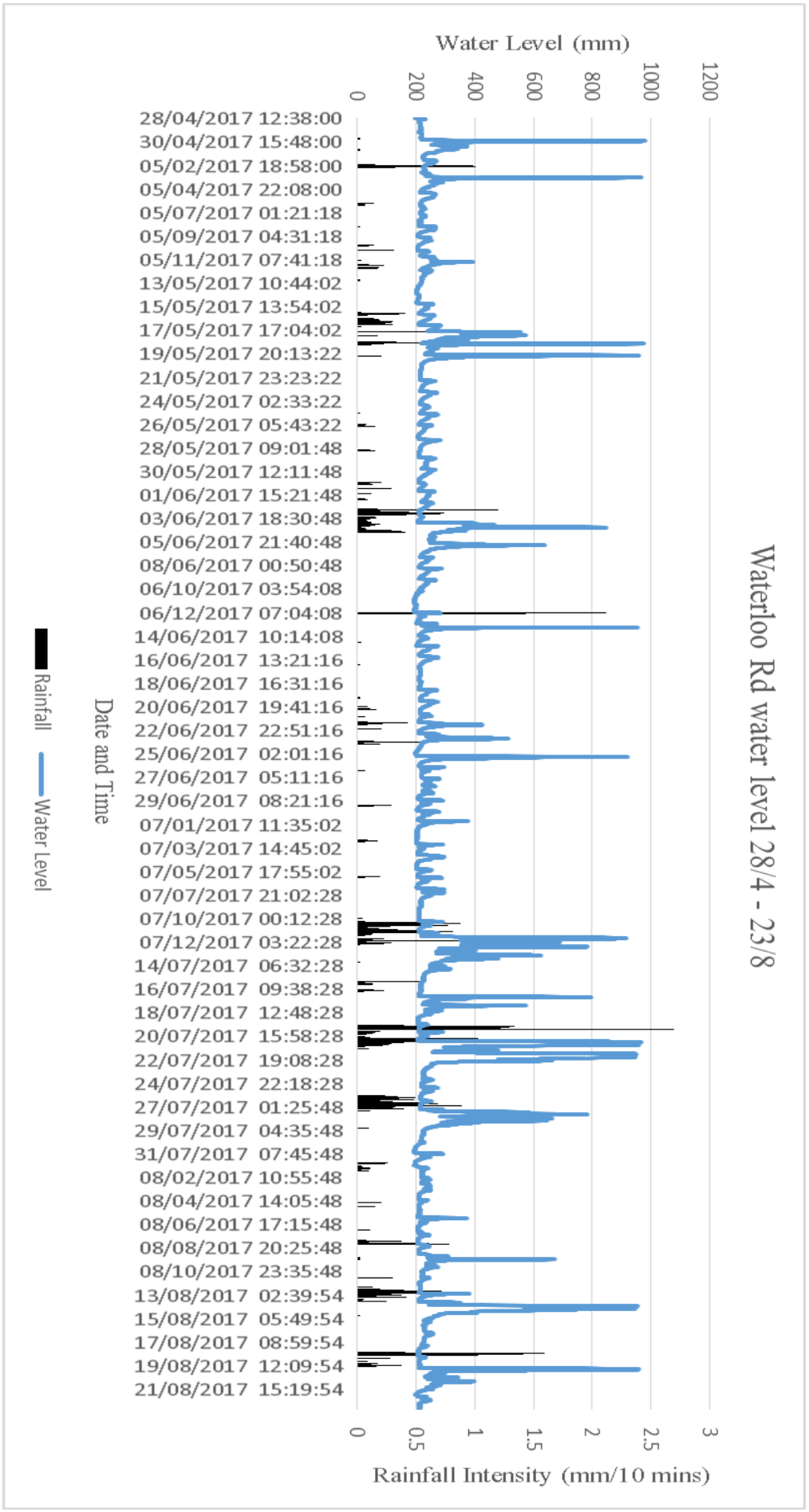


Figure 4.11 Water level at Waterloo Road

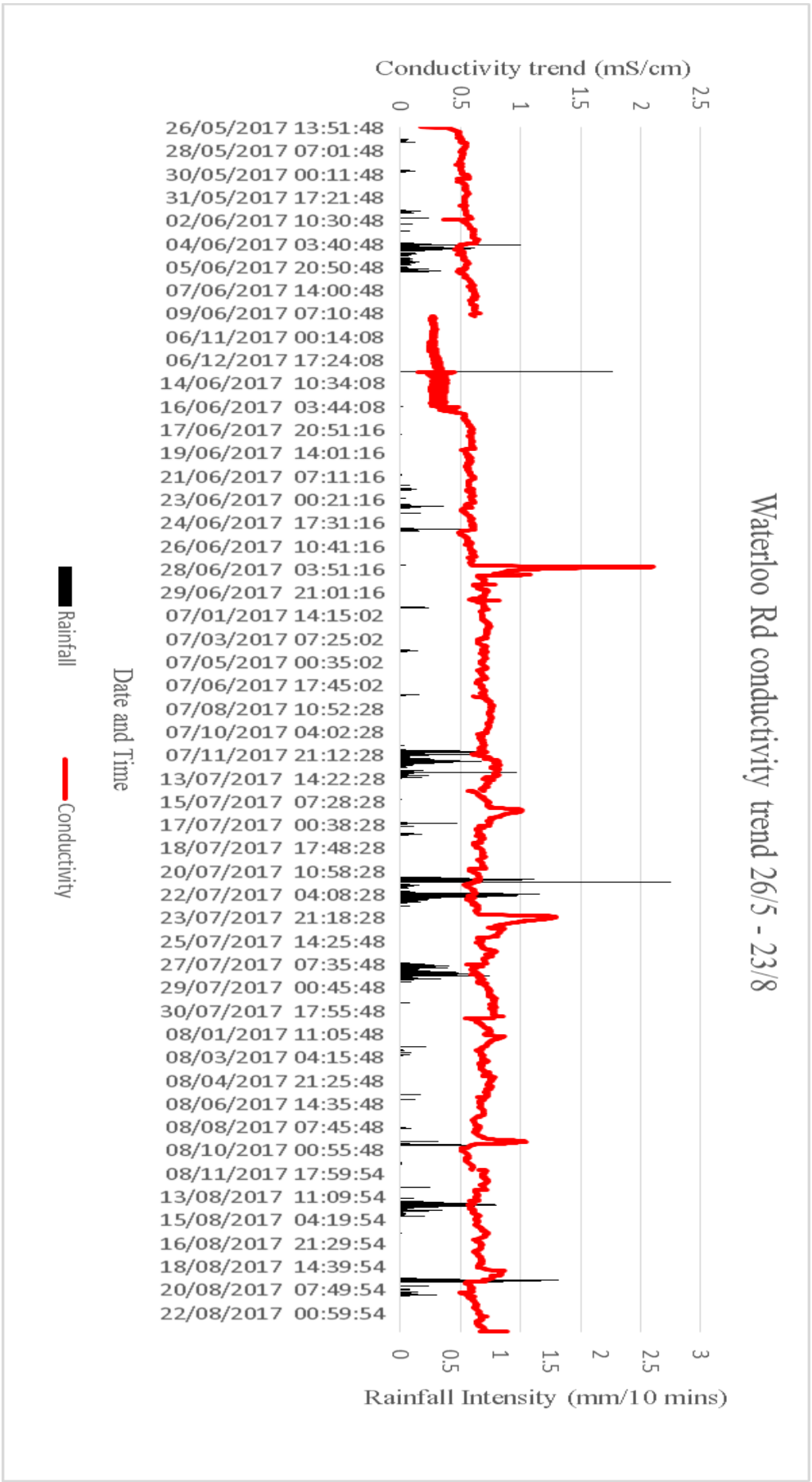


Figure 4.12 Conductivity trend at Waterloo Road

4.3.1.3 Haytons Stream downstream of Washbournes Road

This location was monitored for water level from 28/4/17 to 23/8/17 and conductivity from 26/5/17 to 23/8/17. Loggers were placed downstream of where Haytons Stream re-emerges from the stormwater network at Washbournes Road, in a highly industrial section of the catchment, and immediately after a stormwater pipe that was found discharging in dry weather several times during stream visits.

Water level

This was a very shallow site (water depth ~ 10-30 cm in dry weather) where the stream resembled a channelised box drain, making access more difficult than other sites. Water level peaked at this location when rainfall occurred in the catchment, yet there were occasional very small fluctuations (~20 mm or under) in water level that did occur independent of rainfall (Figure 4.13). This is interpreted to be either from the pipe immediately before the loggers, or from a series of pipes further upstream that drain to the stream, which were occasionally seen trickling into Haytons Stream in dry weather, indicating some form of illicit use of the stormwater network (see Chapter Three for sampling and analysis of discharges). From the water level, these discharges tended to be of very low volume 9which was the case when observed in the field), and did not result in large fluctuations of instream water level, compared to those seen with rainfall in the catchment, or the discharges observed at Waterloo Road. This logger does confirm that the pipe observed discharging in Chapter Three (or one of the series of pipes upstream of this) regularly discharges to the stream in dry weather, indicated by the frequent dry weather fluctuations recorded by the logger at this site. This is important as field observations could only result in observation and sampling of pipes a number of times, yet the logger has successfully recorded evidence of continual frequent discharges when field visits were not possible.

Conductivity

Conductivity appeared to be more variable at this location, and responded (spiked) to rainfall far greater than the upstream site at Waterloo Road. Small to moderate rainfall intensities and events (0.2- 0.4 mm/10 minutes) appeared to result in marked spikes in conductivity at this site compared to sites in the upper or lower catchment (Figure 4.14).

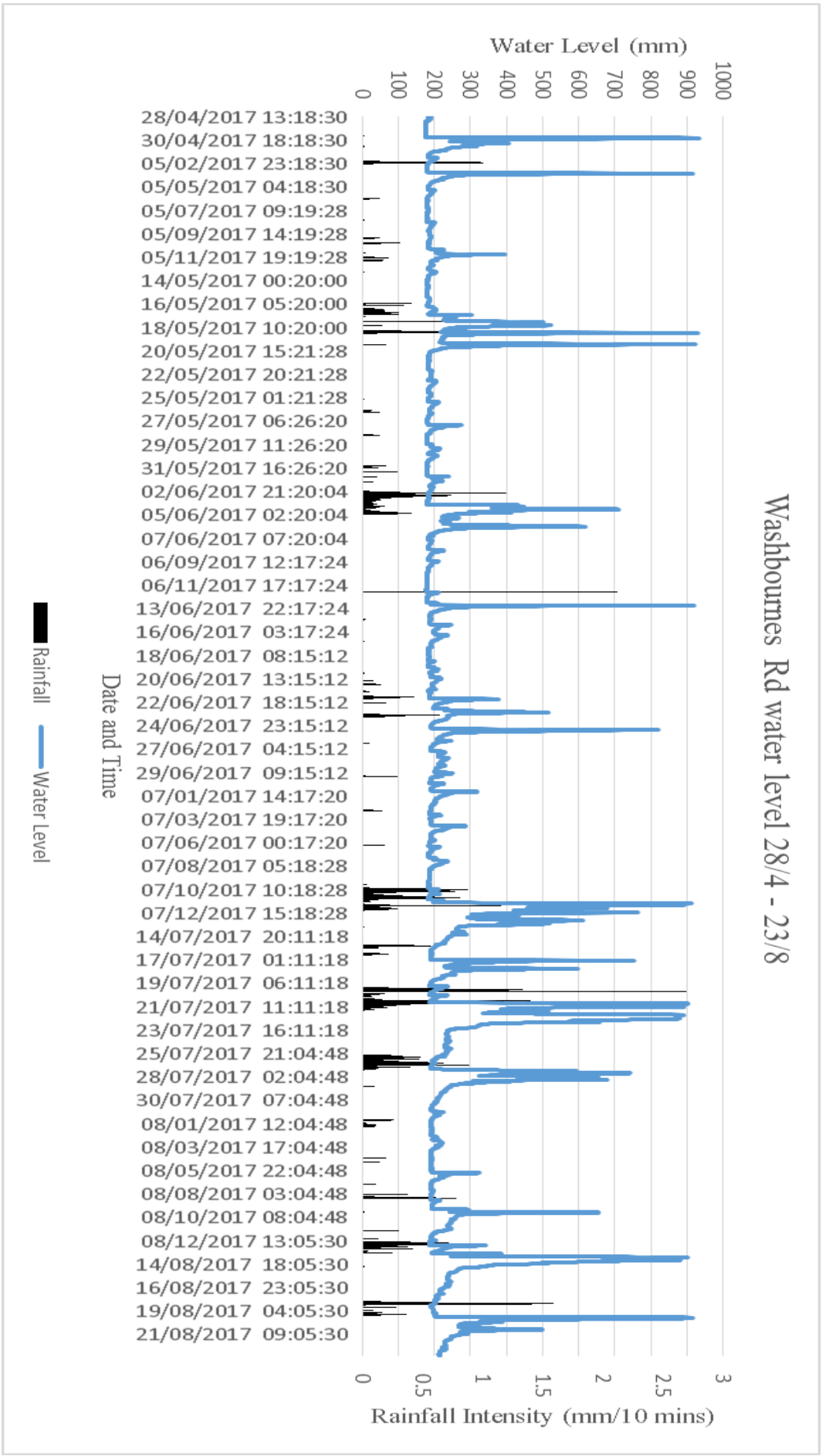


Figure 4.13 Water level at Washbournes Road

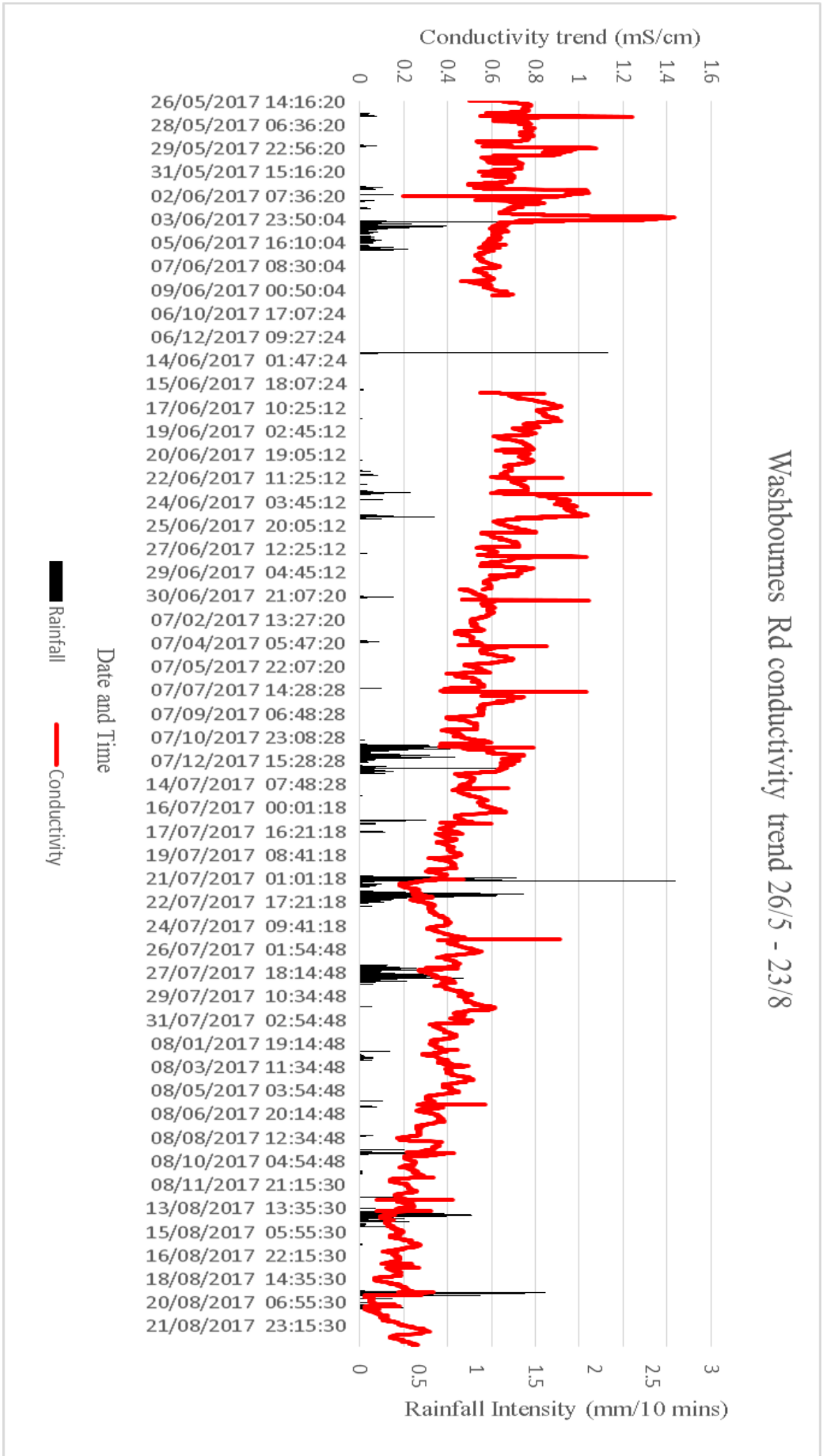


Figure 4.14 Conductivity trend at Washbournes Road

4.3.1.4 Springs Road manhole

This logger, off Springs Road (in the Versatile company car park), was logged for water level from 28/4/17 to 23/8/17. Unfortunately, at this location conductivity logging resulted in data that was continually erroneous, as often the logger would report values of negative conductivity, or other clearly futile data trends, and is thus not reported for this site.

Water level

As with the logger in the Waterloo Road manhole, negative values in the water level logger at this location were interpreted to be incidences of very low/ no flow in the pipes. Figure 4.15 on the following page presents the logger's water level data over the entire logging period matched with rainfall.

At this location, it is clear that rainfall has a strong influence on water level (as it is a stormwater manhole), with almost every spike in water level attributed to rainfall occurring in the catchment. There were several occasions (seen through select weekly water level data in Appendix 5) where water level did display very minute fluctuations independent of rainfall at this site; yet they are so small in magnitude it remains unclear whether these represent active dry weather inputs to the network or simply residual flow within the pipe infrastructure (a common occurrence in the underground network). This manhole was generally characterised with little residual/ stagnant flow present during dry weather, which rapidly spiked during rainfall, and quickly dropped off again to a zero- few mm water depth baseline.

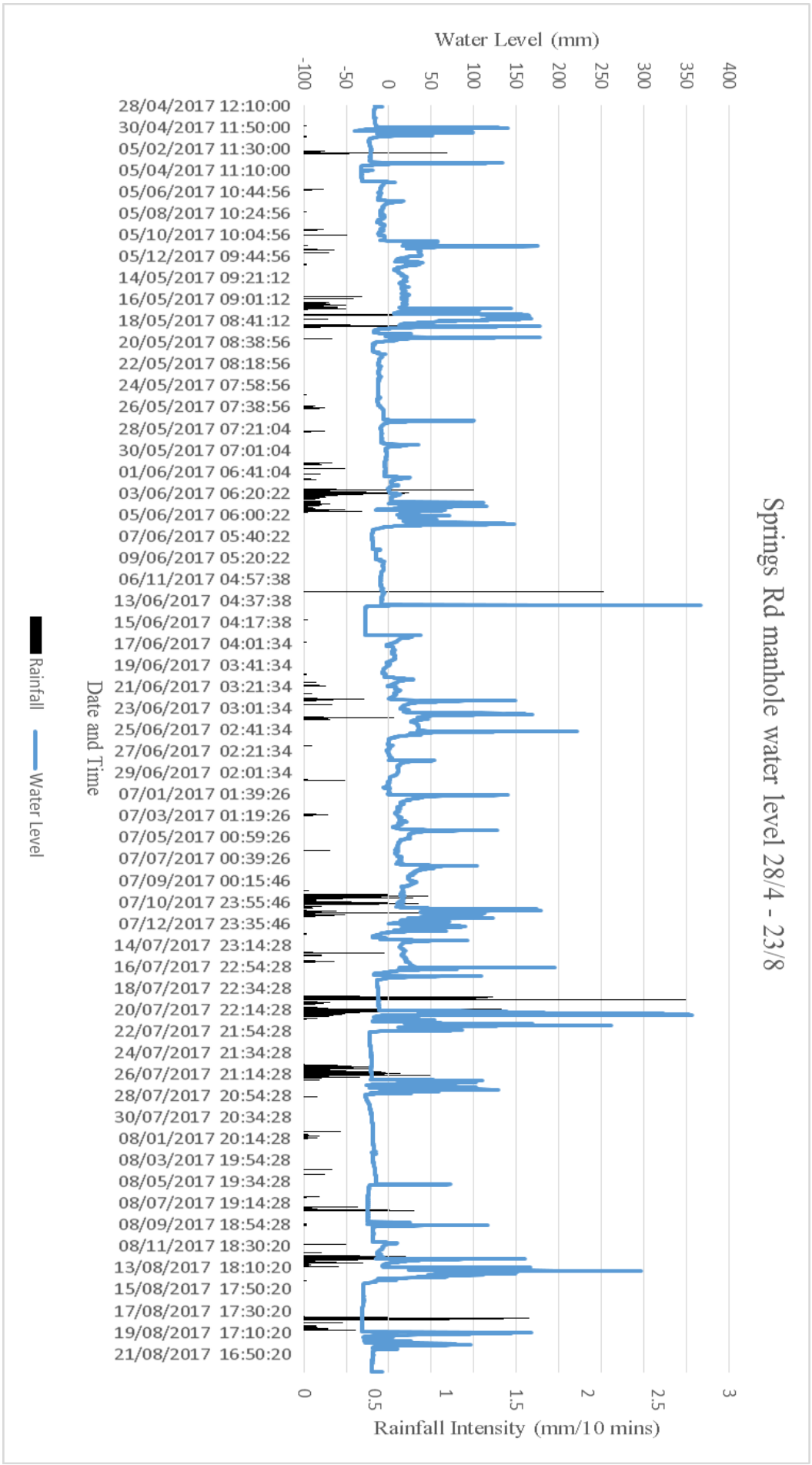


Figure 4.15 Water level in Springs Road manhole

4.3.1.5 Wigram Road stormwater pool

Loggers in this location were monitored for water level from 28/4/17 – 16/6/17 and for conductivity from 19/5/17 – 9/6/17.

Water level

Rainfall at this site was the main control on stream water level, with nearly all incidences of rising water level coinciding with rainfall in the catchment (Figure 4.16). Any appreciable fluctuation in water level after the stormwater pipe was the result of rainfall, appearing to rule out the occurrence of dry weather discharges at this exact location (Figure 4.16). Using additional weekly data in Appendix 5, it is apparent that the water level remained predominantly quiescent in dry weather (at ~300-400 mm depth), with rapid spikes in water level occurring during rainfall, resulting in deeper water levels in the 6, 7 or 800 mm mark depending on rainfall intensity. The pool would slowly drain away after rainfall and usually return to a 300-400 mm baseline. It was due to these consistently stationary water levels and apparent absence of dry weather discharges that these loggers were moved to Gerald Connolly Place on 16/6/17.

Conductivity

The conductivity at this location did not seem to alter substantially during rainfall events in the catchment (Figure 4.17). During rainfall, there were very small fluctuations in conductivity seen at this location, with minor fluctuations occurring during dry weather. This location was a stormwater pooling area that slowly drained into the adjacent Haytons Stream, with the pooling water often stagnant, where dry weather changes in conductivity could be expected. The minor fluctuations in conductivity do not appear to suggest any dry weather discharge (at least at this exact downstream location) during the logging period.

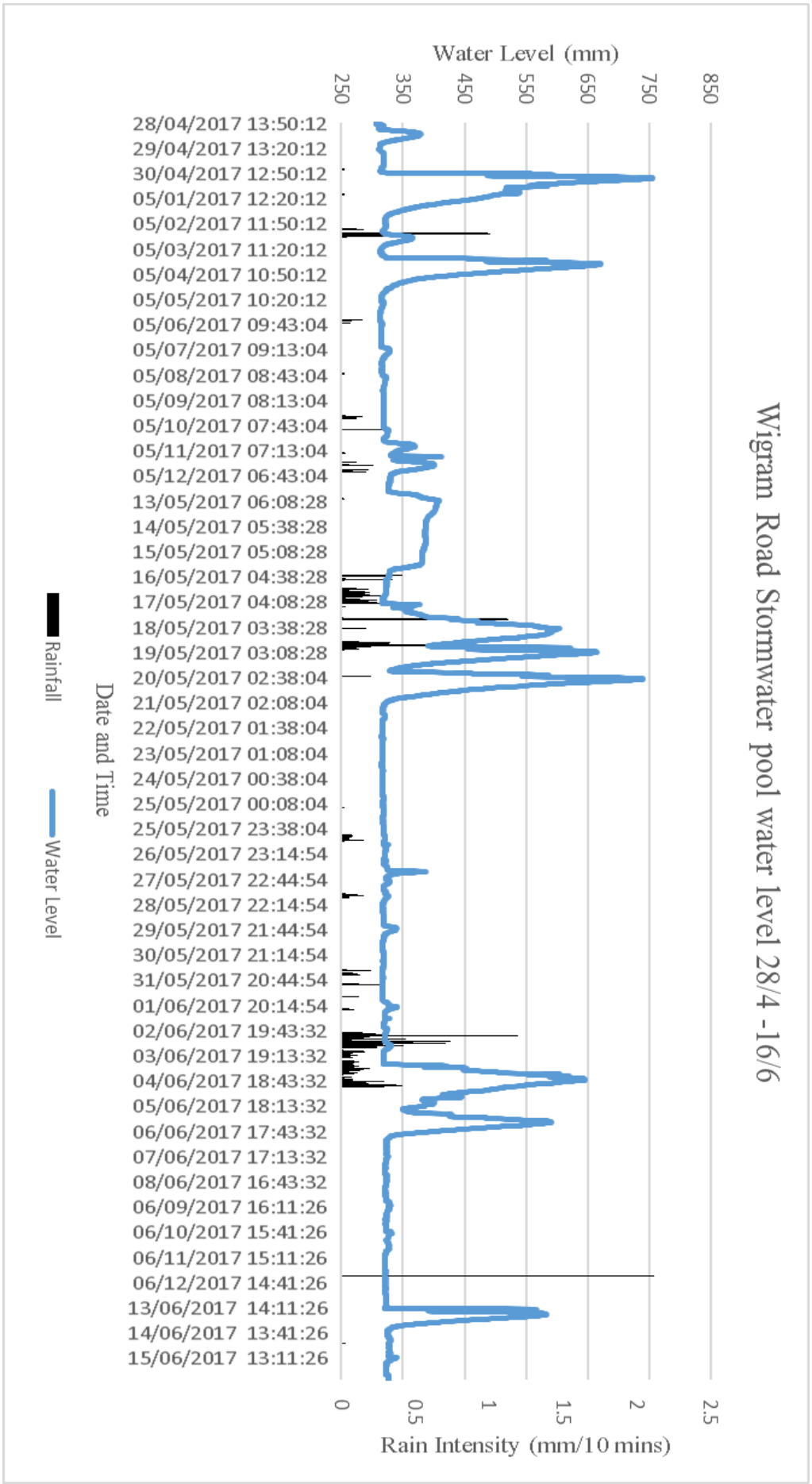


Figure 4.16 Water level at Wigram Road

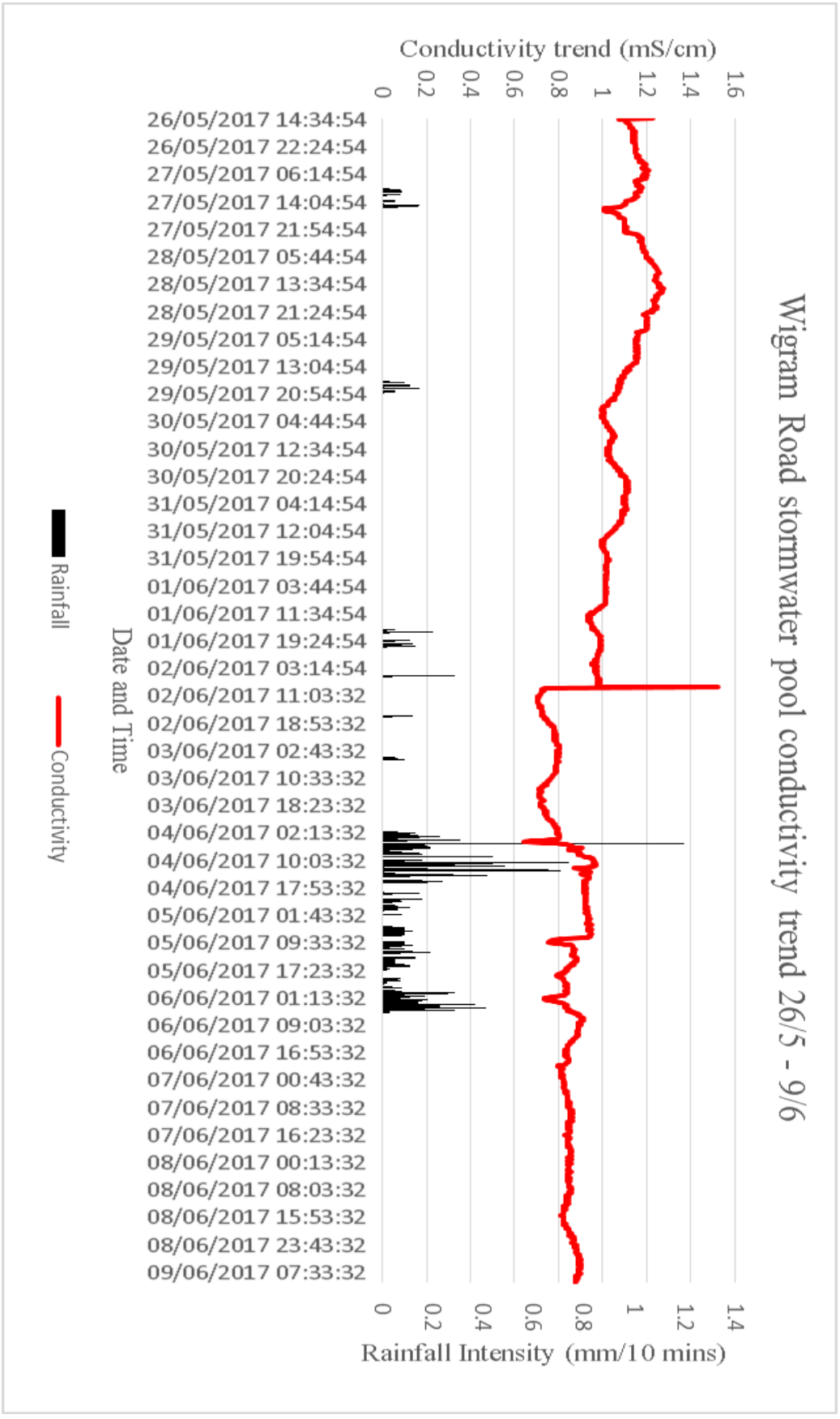


Figure 4.17 Conductivity trend at Wigram Road

4.3.1.6 Haytons Stream at Gerald Connolly Place

This logger set was transferred from the Wigram Road site, successively logging water level and conductivity from 8/7/17 – 23/8/17. This created comparable water level data with O'Sullivan and Charters (2013), to determine if the discharges identified approximately four years ago were still occurring, and for more intensive upper catchment logging.

Water level

Dry weather water level fluctuations were observed at this site (Figure 4.18) and were often similar/ matched those at the first site on Waterloo Road. Dry weather discharges observed were of smaller magnitude and occurrence, suggesting that the fluctuations observed at this site were predominantly sourced from above the stormwater network at Waterloo Road.

Conductivity

Conductivity trend was very variable at this location after the loggers were moved (Figure 4.19), with rainfall appearing to have varied influences on instream conductivity (increases as well as dilutions). It is interpreted that as the loggers had been in-situ at Wigram Road for some time, deposits of silt in the loggers probe holes may have caused minor interference despite cleaning efforts. Additionally, the shallow stream depth at Gerald Connolly Place may have periodically exposed the logger to the open air if the stream water level dropped further, potentially leading to strange dry weather conductivity readings/ fluctuations. As with other locations, additional weekly logger data is provided in Appendix 5.

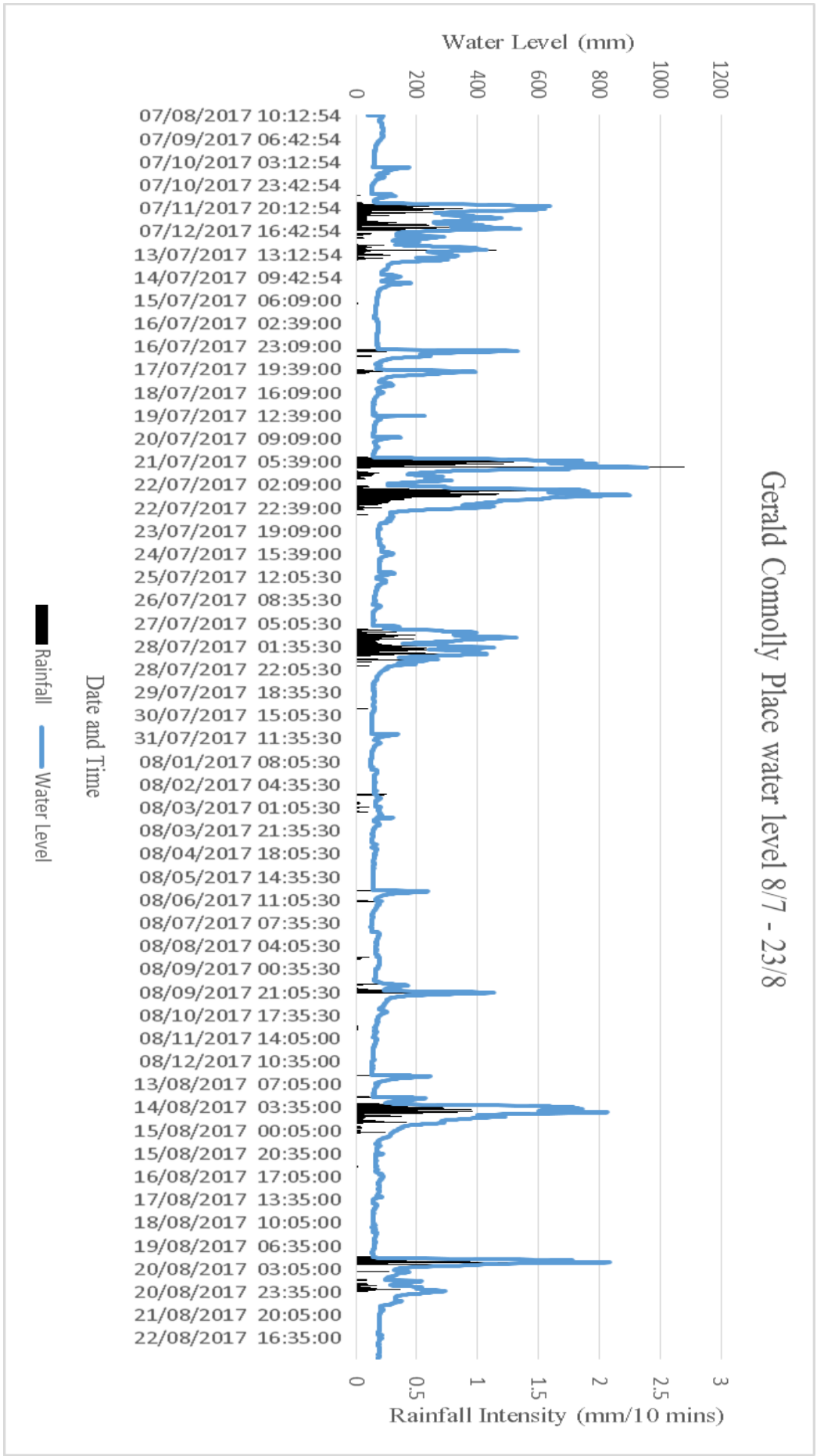


Figure 4.18 Water level at Gerald Connolly Place

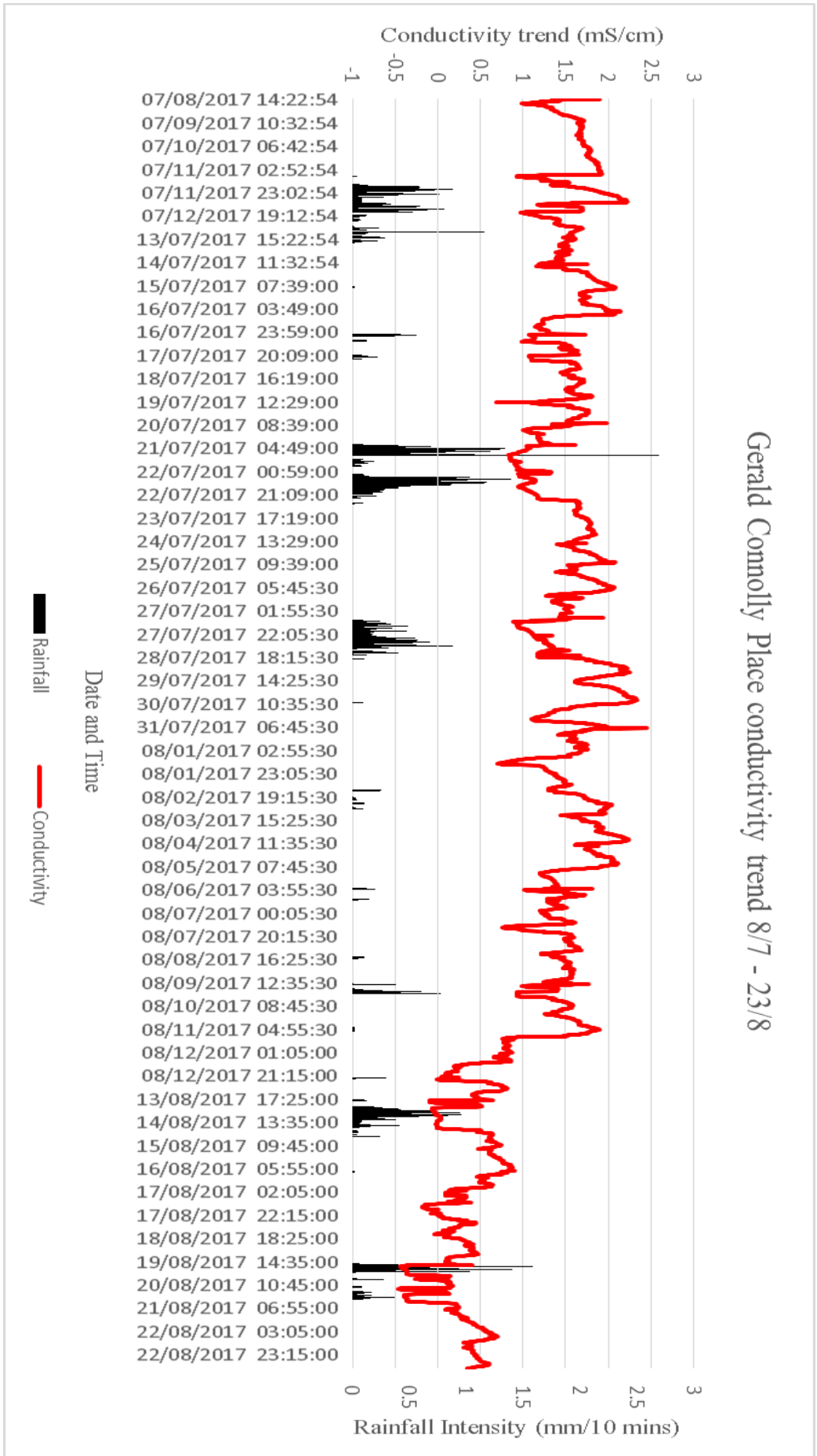


Figure 4.19 Conductivity trend at Gerald Connolly Place

4.3.1.7 Comparison of instream loggers

Loggers both instream and down manholes in the upper and lower catchment were plotted together for water level and conductivity, to illustrate and delineate where individual sources of fluctuation may be sourced from in the catchment.

Water level

As there were very frequent fluctuations in water level passing through the manhole on Waterloo Road, the upper catchment loggers were plotted together to distinguish if this was the source of the continual fluctuations observed in Haytons Stream at Waterloo Road. However as can be seen from Figures 4.20 and 4.21 below, the frequency of fluctuations passing through the manhole on Waterloo Road (recorded by the logger) are much greater and are of a much lower magnitude (size) than those recorded by the logger in Haytons Stream. Additionally, the fluctuations recorded in Haytons Stream at Waterloo Road appear to be of a greater volume (rising the water level to a greater extent). This indicates that although water passing through the manhole on Waterloo Road is likely contributing to some of the regular fluctuations seen in Haytons Stream, there must be other frequent dry weather inputs via the stormwater network occurring along Waterloo Road, either above or below the logged manhole.

Furthermore, when considering the upper catchment data (Figure 4.20), the dry weather fluctuations at Gerald Connolly Place closely match those of the stream at Waterloo Road. This suggests that most of the fluctuations or evidence of dry weather discharges at GCP can be explained or tracked back to the same source from above the stormwater network on Waterloo Road, with the exception of the visible pipe discharge or surface slick described in chapter three.

Logging in the lower catchment (Figure 4.22; of Springs Road manhole, Washbournes Road and Wigram Road) gave similar indications to discharge sources. When comparing the Springs Road manhole to Haytons Stream at Washbournes Road, there are clear water level fluctuations occurring at WBR which are not recorded in the manhole. For the short time Wigram Road was logged, the observed fluctuations at WBR were also not recorded further downstream, indicating that discharges are occurring and sourced from industry at or very close to Washbournes Road. Field visits and site sampling verify this hypothesis, where visible pipe discharges were observed along the box-drain walls of Haytons Stream at Washbournes Road (discussed in Chapter Three). This also indicates that as far as this study has found, no dry weather inputs of appreciable size were recorded in the manhole off Springs Road, suggesting that the dry-weather inputs observed at Washbournes Road were sourced much closer to Haytons Stream in the nearby stormwater network.

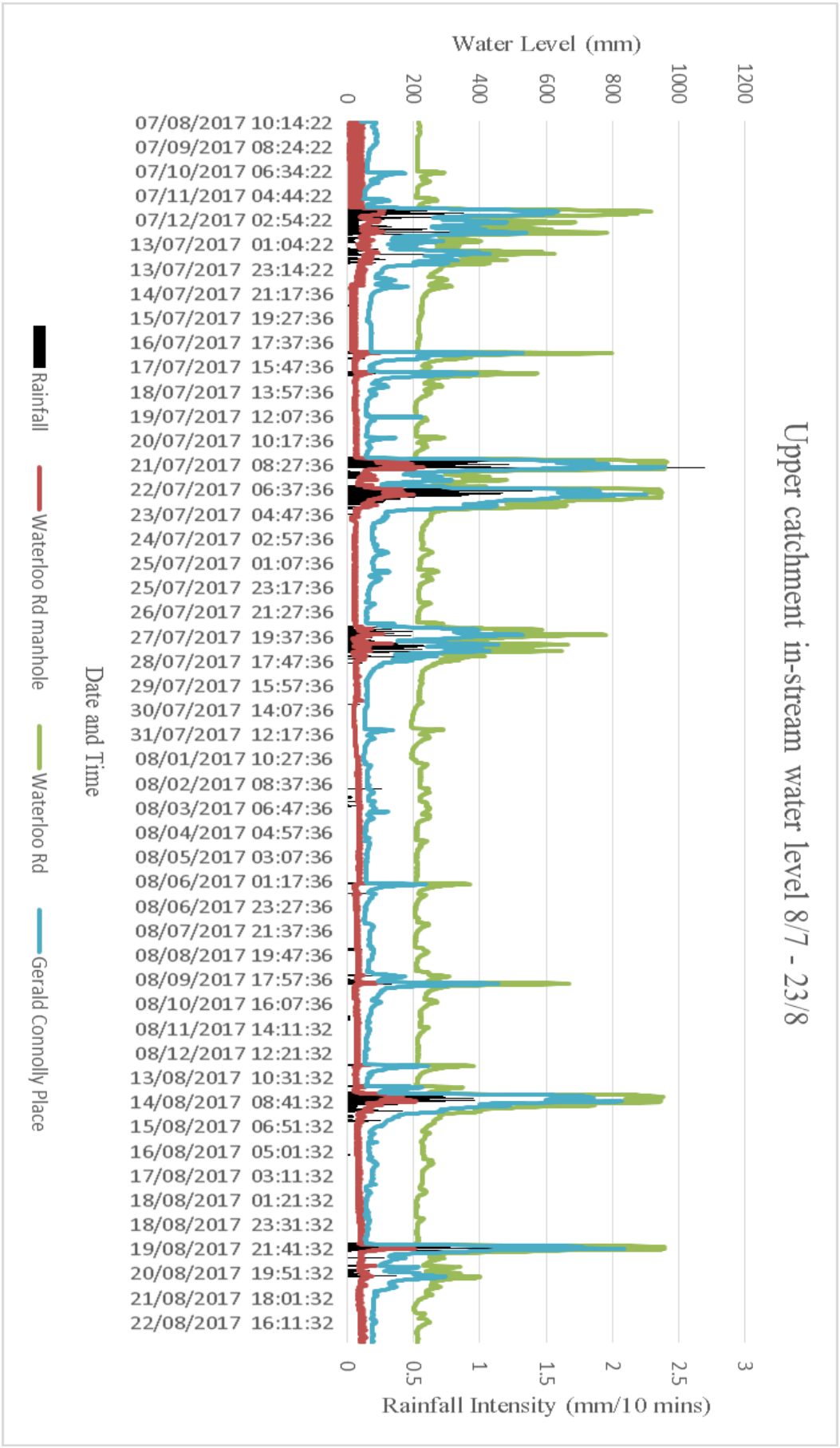


Figure 4.20 Comparison of upper catchment loggers

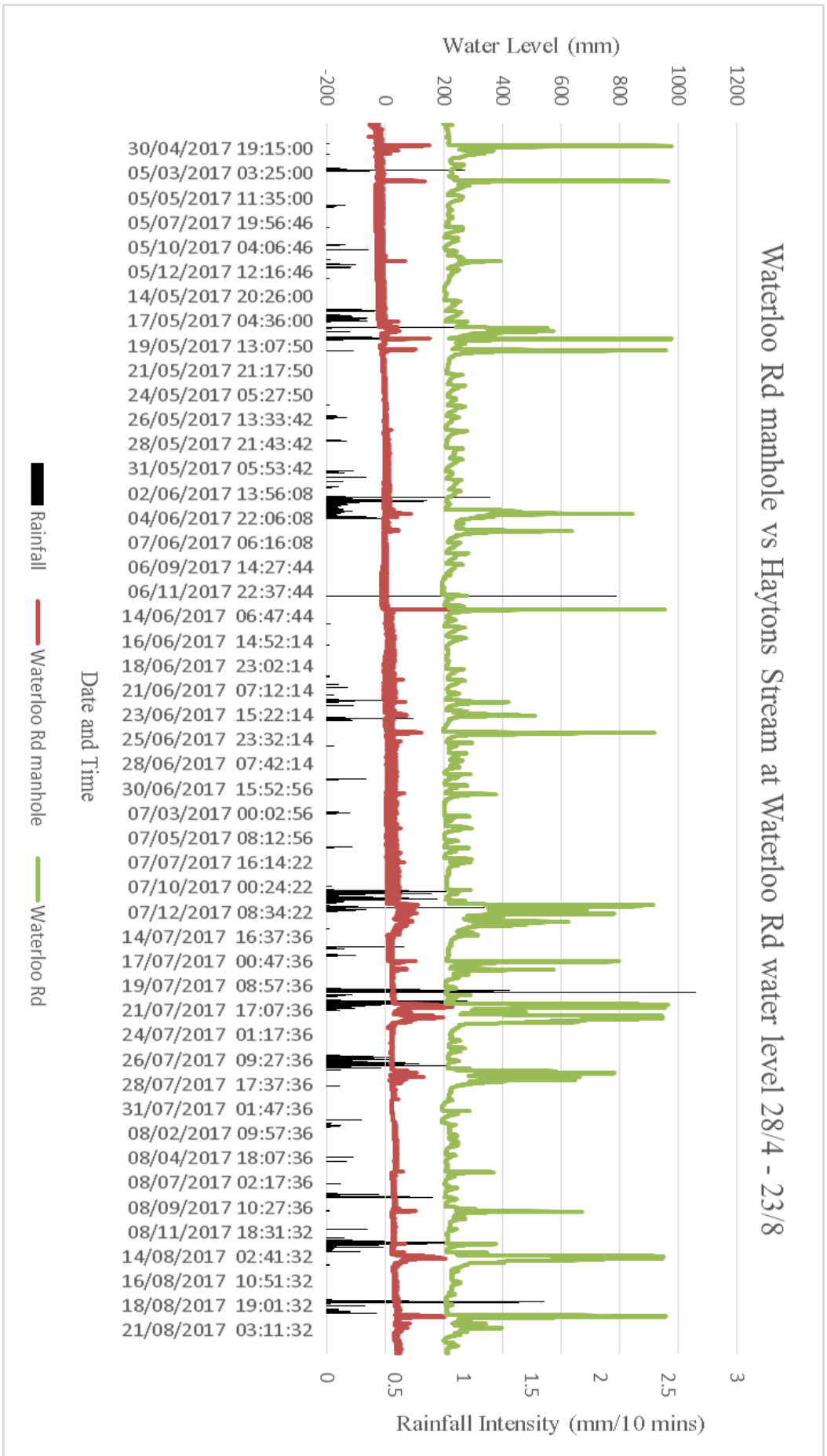


Figure 4.21 Comparison of Waterloo Road manhole and Haytons Stream at Waterloo Road loggers

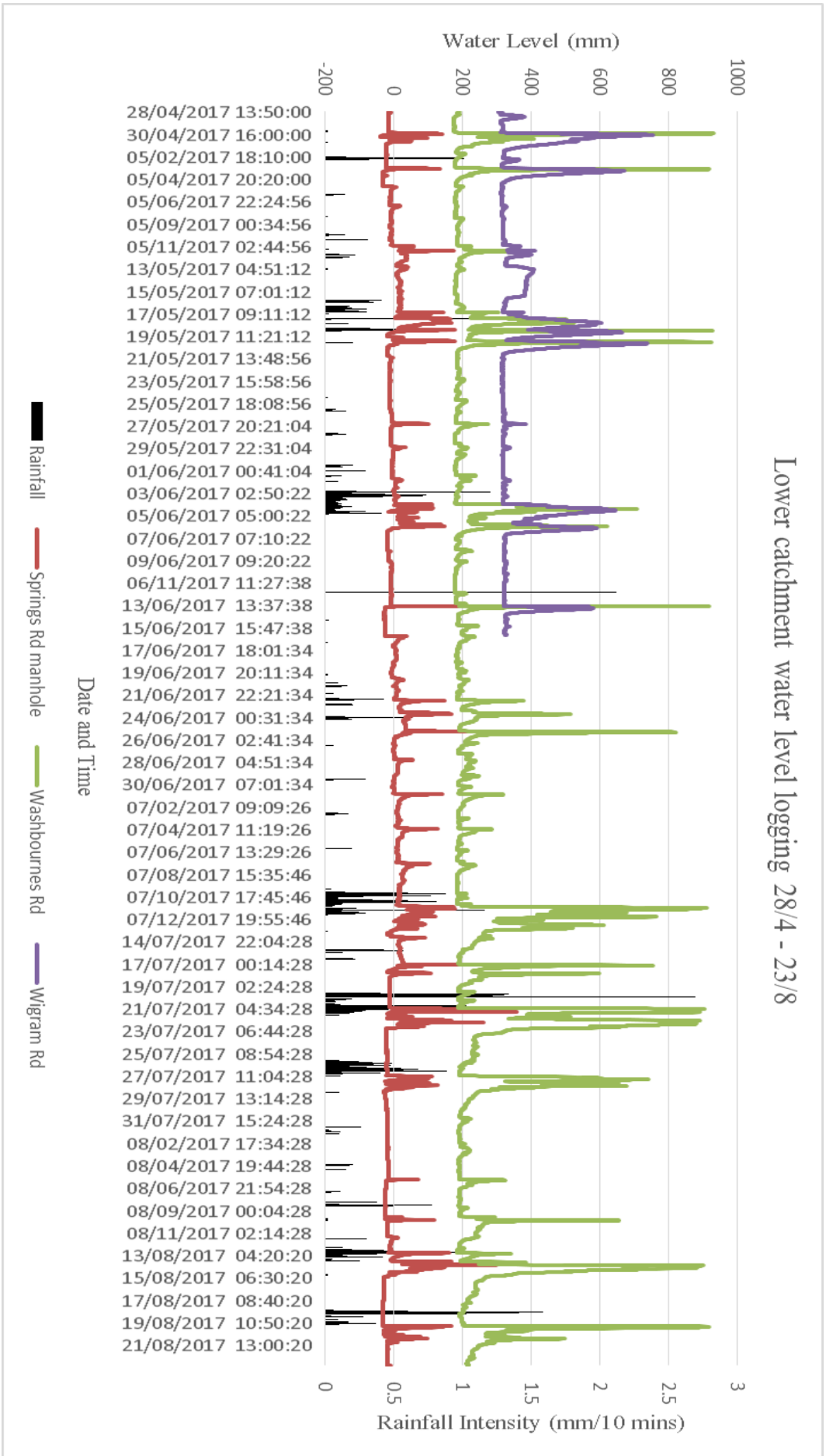


Figure 4.22 Comparison of lower catchment loggers

Conductivity

The three original instream conductivity loggers (WAR, WBR and WGR) were plotted against each other to see how conductivity varied spatially across the catchment (Figure 4.23). Over this series of small rainfall events over a two week period, Haytons Stream responded differently to rainfall depending on the individual site across the catchment. On Figure 4.23 below (and using the weekly logging data from Appendix 5), Waterloo Road conductivity tends to be diluted/ stationary in rainfall events, with the instream conductivity trend tending to decrease or remain very similar with rainfall in the catchment. The same tended to occur at Wigram Road, where rainfall would not drastically alter conductivity recorded by the logger. However Washbournes Road appears different, where even successively small intensities of rainfall (~0.2 mm/10 minutes) appear to cause large spikes in the stream conductivity trend, which rapidly drop back off again after rainfall has ceased. This is picked up both when plotting instream conductivities together, and when consulting weekly/long-term conductivity logging at Washbournes Road alone. As can be seen in the conductivity logger at Washbournes Road, the conductivity spiked largely with any sufficient rainfall in the catchment (i.e. enough rainfall to generate a runoff), further suggesting the notion from chapter three that there is some activity/ industry in the mid catchment responsible for these rainfall/wash-off-driven spikes in conductivity, which were not regularly seen at such magnitudes in the upper or lower catchment sites. It should be noted that the spike in ‘dry weather’ in the middle of the graph was due to removal of loggers for downloading of data.

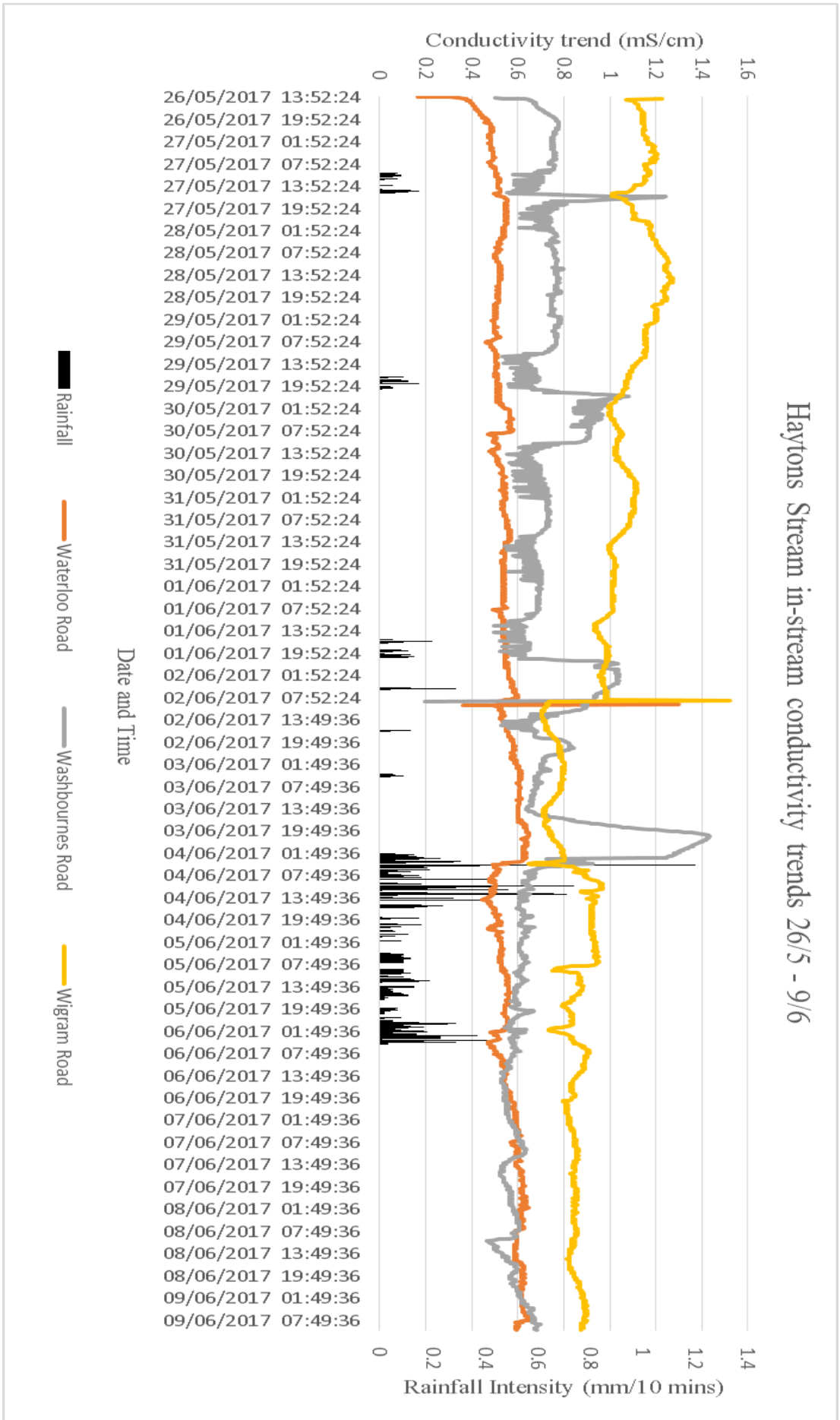


Figure 4.23 Comparison of in-stream loggers' conductivity trends

4.3.2 Sump sampling

4.3.2.1 Rainfall data

Stormwater sumps were sampled over four separate sampling days due to the number of sites visited and time taken to sample. The dates of each sampling run, and relevant meteorological data for those days is provided in Table 4.4.

Table 4.4 Antecedent Dry Days on sump sampling campaigns

Sumps sampled	ADD	Notes:
Sumps 1-4: 4/7/17	3	On 4/7/17 ADD would be 9 if ignoring rainfall <1.2 mm
Sumps 4-6: 30/8/17	9	
Sump 7: 5/9/17	3	
Sumps 8-9: 2/10/17	10	

4.3.2.2 Physio-chemical data

The physio-chemical data for all sampled sumps is provided in Table 4.5 below. The pH ranged from 6.76- 8.85 across the nine sumps. Dissolved Oxygen (DO) was consistently low across sumps, ranging from 1.05 mg/L (9.6%) - 9.12 mg/L (78.8%). Conductivity ranged between 0.02- 294 µS/cm, with most sumps between 100-200 µS/cm. Sump water temperatures ranged from 8.7- 15.6 ˚C.

Table 4.5 Physio-chemical data from sampled sumps

Sump	pH	Temperature (˚C)	Dissolved Oxygen (mg/L & % saturation)	Conductivity (µS/cm)
1	6.81	10.9	1.05 (9.6%)	199
2	6.76	11.5	6.53 (60.3%)	0.02
3	7.16	10.1	6.11 (54.6%)	177
4	7.13	8.7	9.12 (78.8%)	205
5	7.64	11.6	3.60 (33%)	294
6	7	10.9	2.09 (18.5%)	201
7	8.85	12.3	6.05 (57.8%)	110
8	7.72	15.6	1.26 (12.8%)	197
9	7.26	14.5	2.58 (28%)	234

4.3.2.3 Total Suspended Solids

The full table of all analysed parameters in all sumps is provided in Appendix 6. TSS concentrations in sampled sumps are presented below in Figure 4.24. Sump 5's TSS container was broken during transportation and was therefore unable to be analysed. The highest TSS concentration was at sump 2, where significant contamination was present (concentration of 2860 mg/L). The lowest concentration was in sump 8 (4 mg/L), whereas the mean of all sampled sumps was 545 mg/L (yet the median was 129.8 mg/L due to a high concentration in sump two).

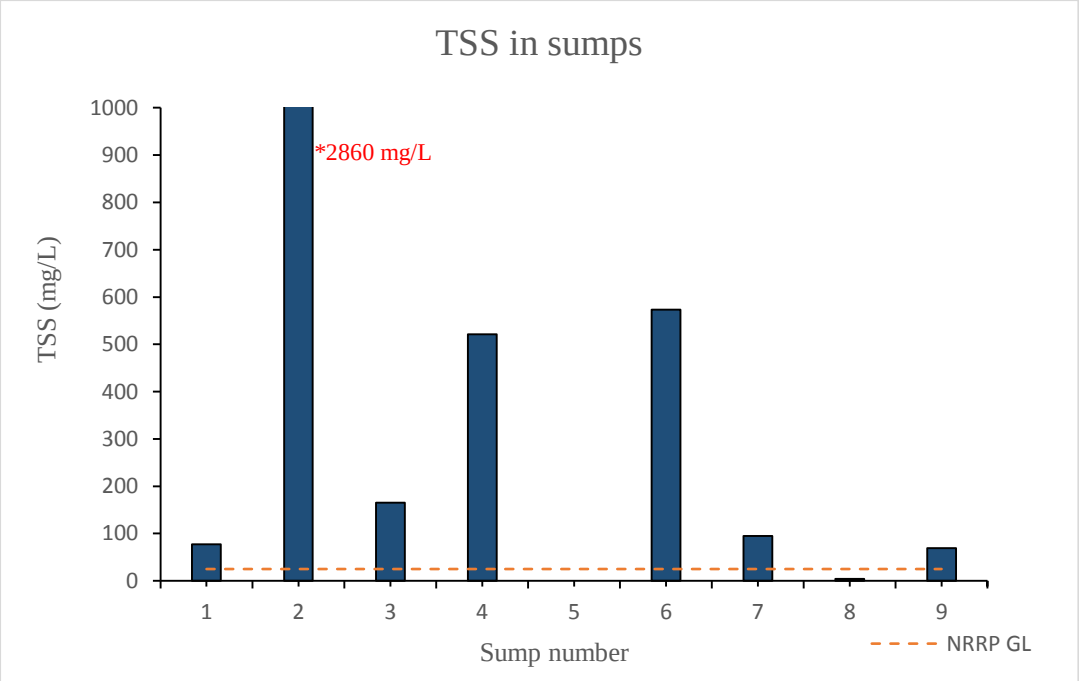


Figure 4.24 TSS in sampled sumps

4.3.2.4 Total trace elements

Total trace element concentrations were compared to ANZECC 80% species guidelines where applicable. No metals exceeded the CCC trade waste bylaw for the sewer network, yet many were still elevated above ANZECC species protection guidelines (Figure 4.25).

Aluminium

Al was elevated in all sampled sumps in the catchment (Figure 4.25), with all but one sump (sump eight) exceeding the ANZECC 80% guideline. The highest Al concentration was in sump two (37,657 µg/L) and the lowest was in sump eight (121 µg/L). The average sump Al concentration across all nine sumps was 14,391 µg/L, whereas the median was 2974 µg/L.

Arsenic

All sumps had As concentrations less than the ANZECC 90% freshwater guideline of 42 µg/L. The maximum As concentration was in sump five (39.8 µg/L) whereas the minimum was in sump eight (1.59 µg/L). Average and median arsenic across all sumps was 12.6 and 6.26 µg/L respectively.

Cadmium

Three sumps (two, five and six) exceeded the ANZECC 80% guideline for Cd. The maximum Cd was found in sump two (37 µg/L) whereas the minimum was in sump eight at 0.13 µg/L. Average Cd was 4.98 µg/L across all sumps, yet median concentration was 0.52 µg/L.

Chromium

The 40 µg/L ANZECC 80% guideline for Cr was exceeded twice, in sumps two and five. Sump two had the maximum Cr concentration of 237 µg/L, whereas the minimum concentration of 1.78 µg/L was found in sump eight. The average Cr concentration in all sumps was 50.5 µg/L, and the median was 12.4 µg/L.

Copper

Cu was elevated in all sampled sumps, with all sumps elevated in concentration above the 80% ANZECC freshwater guideline of 2.5 µg/L. Sump two had the maximum observed Cu concentration of 989 µg/L, and the minimum Cu concentration of 7.67 µg/L was in sump eight. Average and median copper in all sumps were 212 and 119 µg/L respectively.

Lead

Pb concentrations were above the 80% guideline in seven sumps. The highest Pb was found in sump two at 620 µg/L, with the lowest in sump one (6.18 µg/L). Average lead across all sumps was 140 µg/L, whereas the median concentration was 45 µg/L.

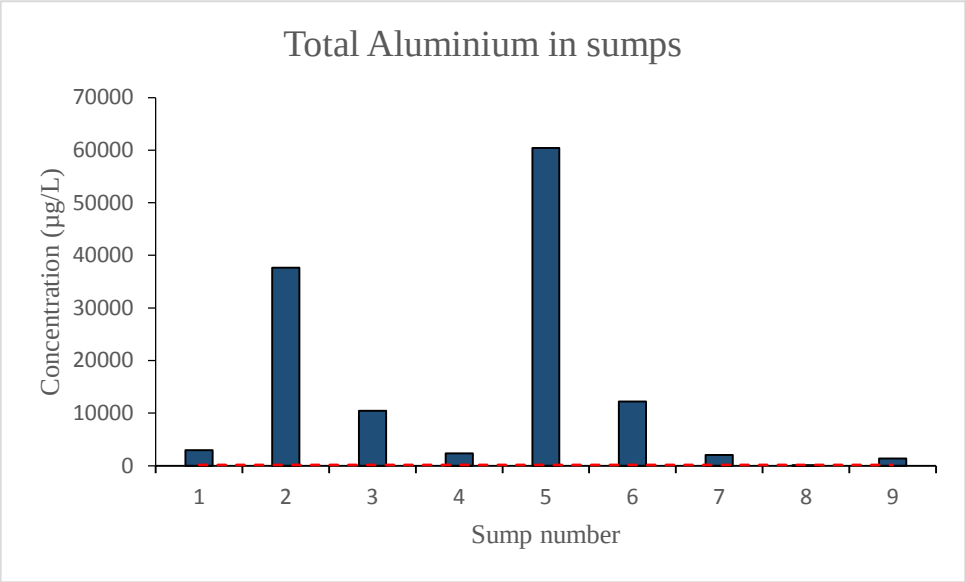
Nickel

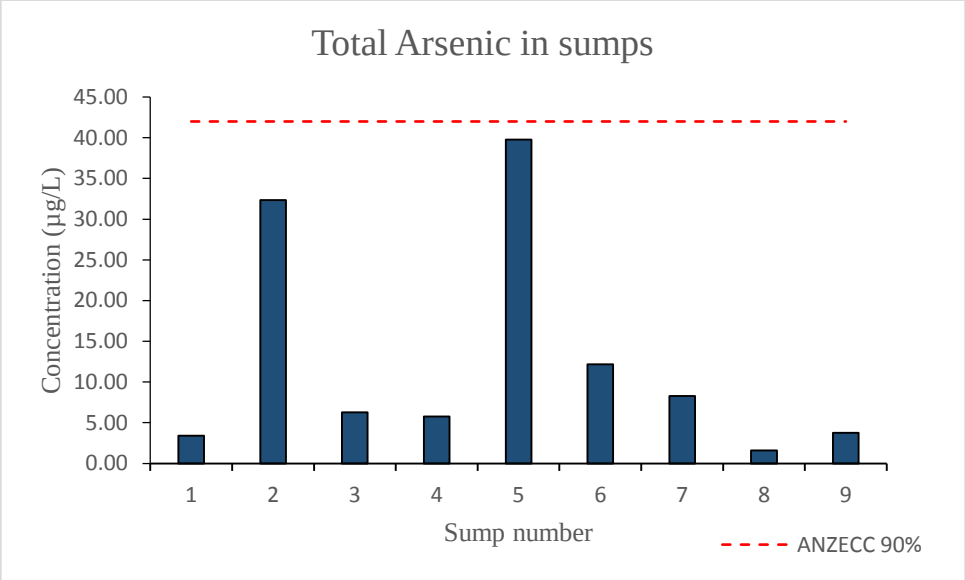
Three of the sampled sumps (two, five and six) exceeded the 80% guideline for Ni of 17 µg/L in the catchment. Sump two held the maximum concentration of 374 µg/L whereas sump eight had the minimum of 2.6 µg/L. Overall average and median Ni concentrations were 57.9 and 12.4 µg/L respectively.

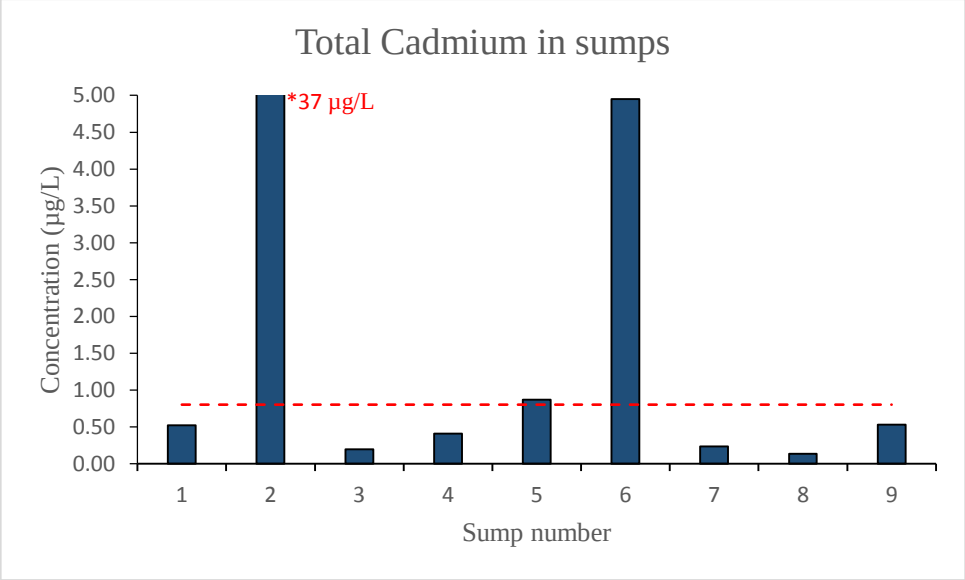
Zinc

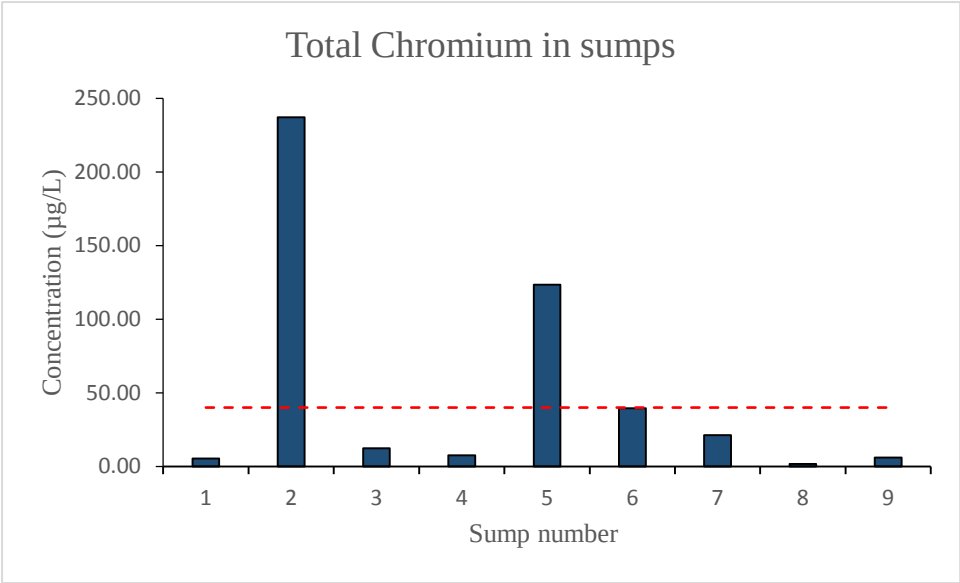
Zn was highly elevated across all sampled sumps, with all sumps exceeding the ANZECC 80% guideline of 31 µg/L. Sump two held the maximum Zn concentration of 35,286 µg/L, whereas the

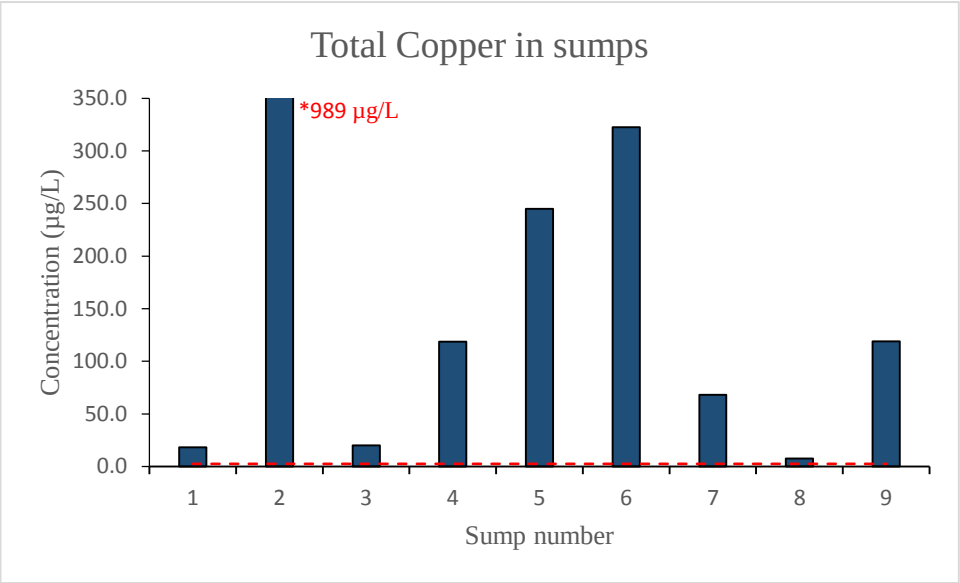
minimum Zn concentration was in sump three at 221 µg/L. Average zinc across all sumps was 4823 µg/L and median zinc was 599 µg/L.








Total Chromium in sumps
Concentration (µg/L)
250.00
200.00
150.00
100.00
50.00
0.00
1
2
3
4
5
6
7
8
9
Sump number


Total Copper in sumps
*989 µg/L
Concentration (µg/L)
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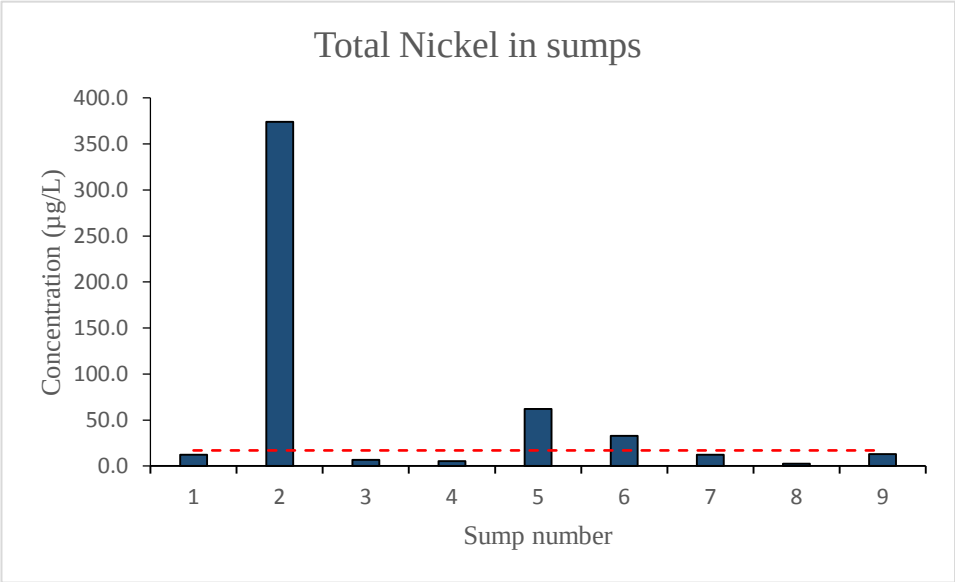
300.0
250.0
200.0
150.0
100.0
50.0
0.0
1
2
3
4
5
6
7
8
9
Sump number


Total Nickel in sumps
Concentration (µg/L)
400.0
350.0
300.0
250.0
200.0
150.0
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50.0
0.0
1
2
3
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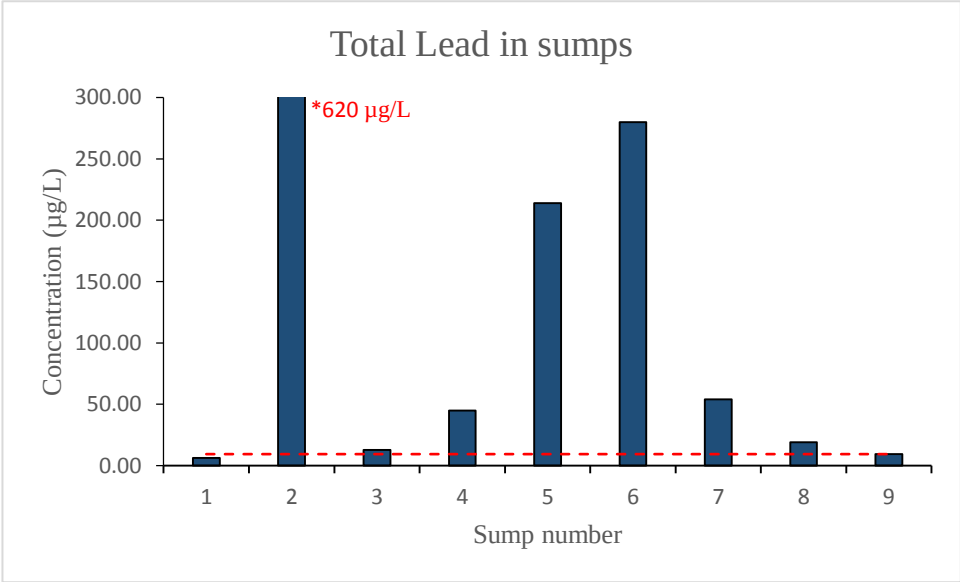
9
Sump number


Total Lead in sumps
*620 µg/L
Concentration (µg/L)
300.00
250.00
200.00
150.00
100.00
50.00
0.00
1
2
3
4
5
6
7
8
9
Sump number

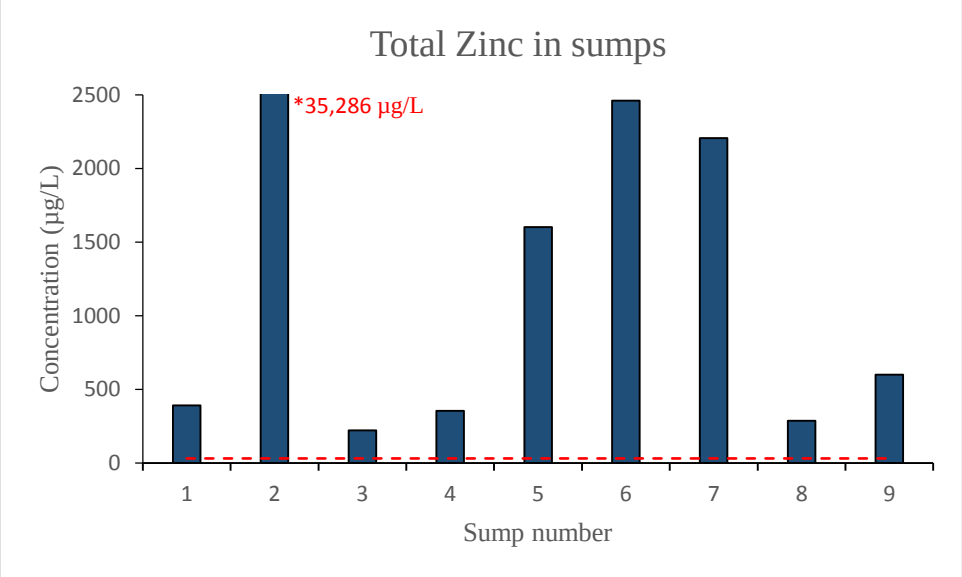


Figure 4.25 Total trace elements in sampled sumps

4.3.2.5 Nutrients

Nitrogen species concentrations in all sumps are provided in Figure 4.26, whereas phosphorous species results are presented in Figure 4.27. Dashed red lines represent ANZECC trigger values for relevant nutrients.

Ammoniacal-N

Ammoniacal-N was highest in sump one, with a concentration of 2.9 mg/L. The lowest concentration was in sump seven (0.01 mg/L), and the average concentration across all sampled sumps was 1.15 mg/L.

NNN

The mean NNN concentration across the sumps was 0.52 mg/L, with the highest concentration (1.56 mg/L) in sump eight, and the lowest concentration in sump two (0.022 mg/L).

TKN & TN

Total Kjeldahl Nitrogen was highest in sump two, with a concentration of 17 mg/L, and lowest in sump seven (1.48 mg/L). Consequently, Total Nitrogen was also highest in sump two (17 mg/L) and lowest in sump seven (2.02 mg/L). The average TKN across sumps was 6.59 mg/L, whereas the average TN concentration was 7.11 mg/L, substantially above the 0.614 mg/L ANZECC trigger value.

DRP & TP

Average Dissolved Reactive Phosphorous was 0.27 mg/L and was highest in sump five (0.99 mg/L). The lowest DRP concentration was found in sump six (0.013 mg/L). Total Phosphorous averaged 1.48 mg/L in all sampled sumps, with the highest concentration found in sump five at 5.2 mg/L. The lowest TP (0.098 mg/L) was in sump eight, yet this value is still elevated beyond the ANZECC trigger of 0.033 mg/L.

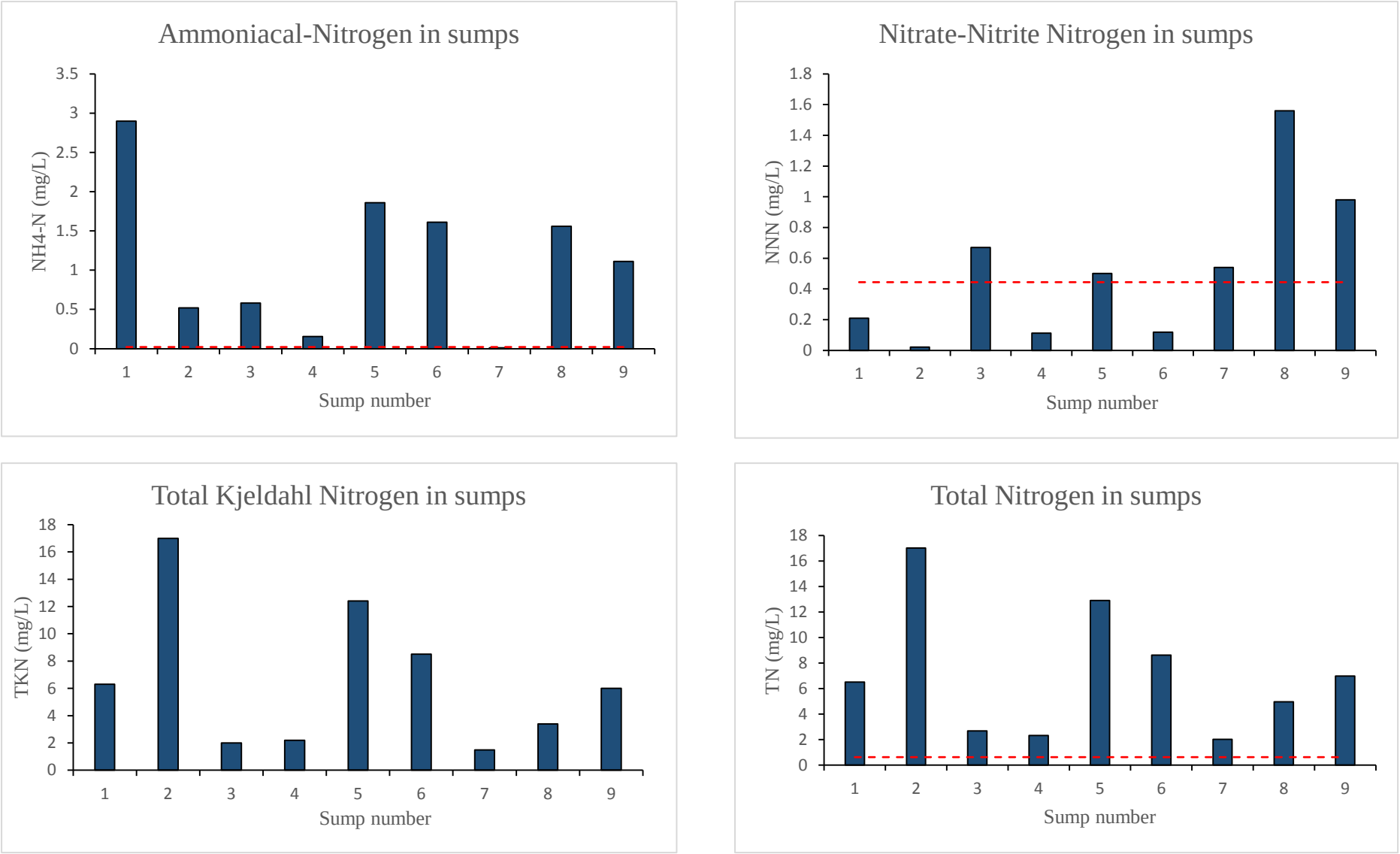
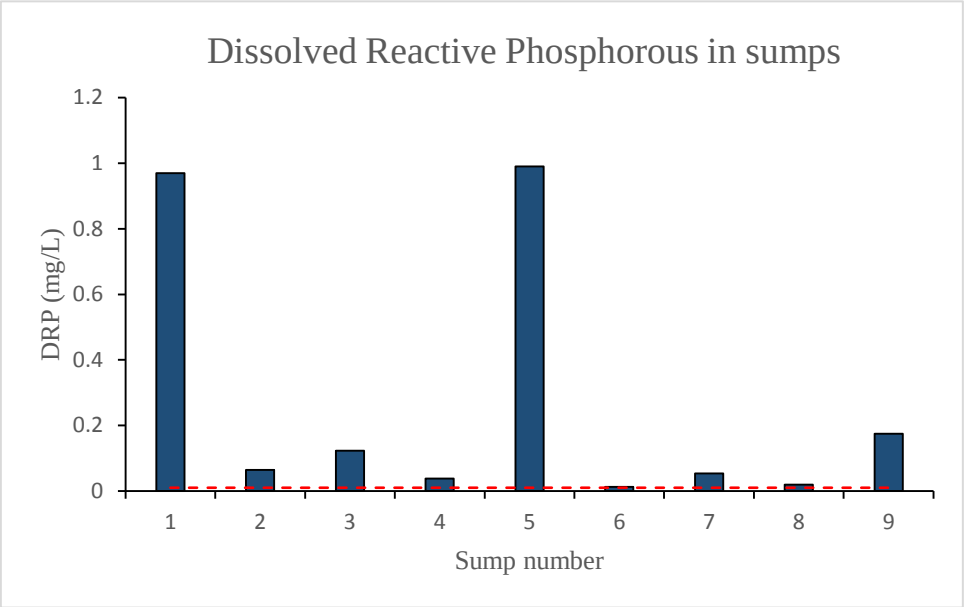


Figure 4.26 Nitrogen species in sampled sumps



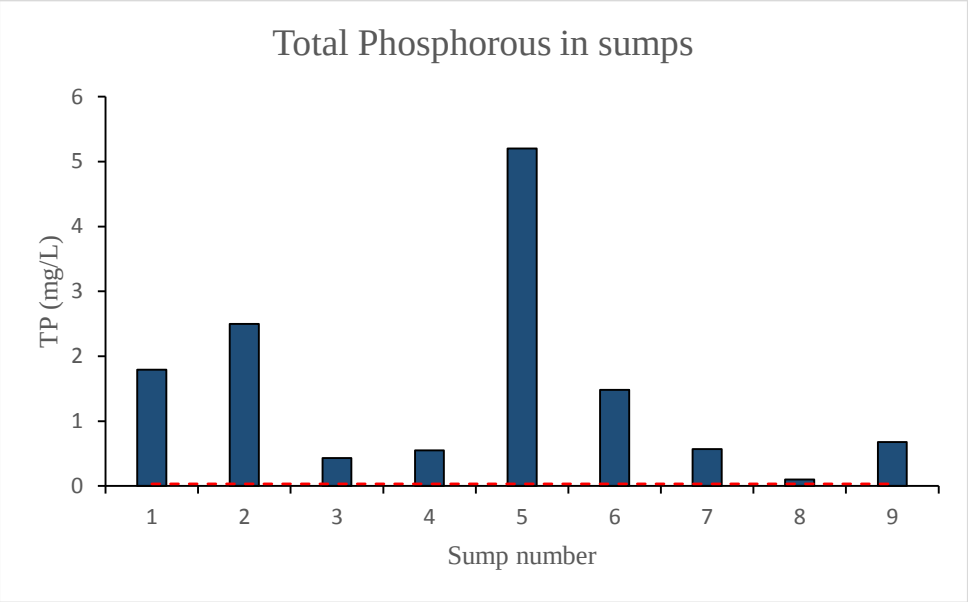


Figure 4.27 Phosphorous species in sampled sumps

4.3.2.6 Organic contaminants and microorganisms

Microorganism and hydrocarbon results for all sampled sumps are presented in Tables 4.6 and 4.7, whilst Figure 4.28 presents the Chemical Oxygen Demand (COD) results for each sump. Volatile Organic Compounds were mostly below detection limits across the nine sumps. Compounds that were detected were far below their relevant ANZECC guideline (see Appendix 6 for all VOC's detected in sumps).

Table 4.6 Microorganism content in sampled sumps

Microorganisms in sumps			
Sump	Tot. Coliforms	Fec. Coliforms	*E. Coli*
	MPN/100 ml	CFU/100 ml	MPN/100 ml
1	>2420	900	687
2	>24200	4100	461
3	>2420	n/a	308
4	>2420	n/a	>2420
5	>2420	140	9
6	2420	<10	<1
7	53	<1	1
8	1203	<10	1
9	>2420	10	22

Table 4.7 Total Petroleum Hydrocarbons in sampled sumps

Hydrocarbons in sumps				
Sump	C7-C9	C10-C14	C15-C36	TPH
	mg/L	mg/L	mg/L	mg/L
1	<0.06	<0.2	<0.4	<0.7
2	1.6	26	25000	25000
3	<0.06	<0.2	0.8	0.8
4	<0.06	39	910	950
5	<0.06	<0.2	<0.4	<0.7
6	<0.06	<0.2	<0.4	<0.7
7	<0.06	<0.2	<0.4	<0.7
8	<0.06	<0.2	<0.4	<0.7
9	<0.06	<0.2	0.9	0.9

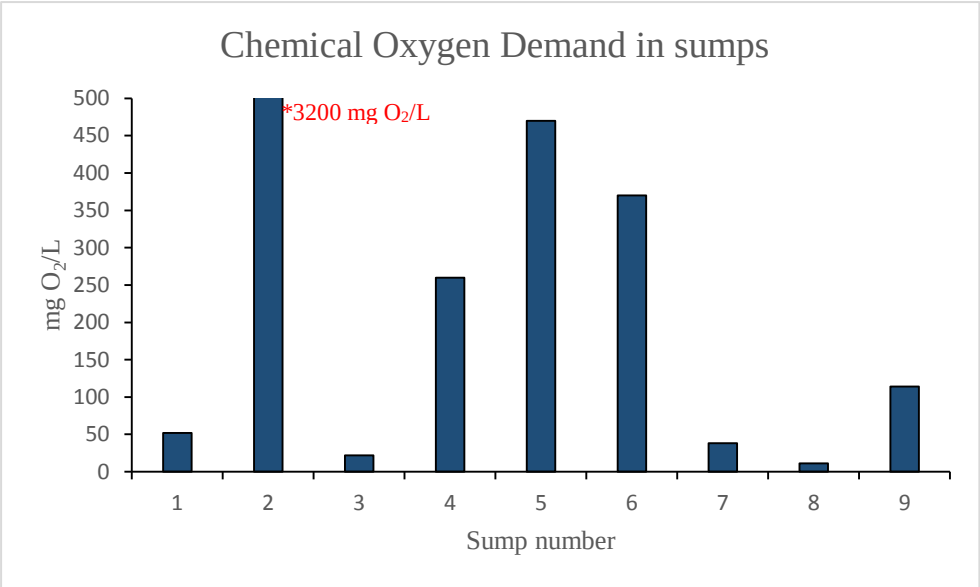


Figure 4.28 Chemical Oxygen Demand in sampled sumps

4.3.2.7 Contaminant ranking/ sump grouping by industry operations

The relative levels of sump contamination from important sampled pollutants were crudely ranked either high, medium or low; based on the level of exceedance of a guideline and concentrations relative to other sumps. Contaminants were then compared relative to the industry type, to present an indication as to what industries may be responsible for certain contaminants found in the receiving environment of Haytons Stream (Table 4.8). For example, it is clear that most industries visited in this industrial catchment have contributed high TSS concentrations to the network, regardless of the nature of industry. Ammoniacal-N, Total-N and DRP were generally elevated in all sumps, whilst *E. coli* was high in the first four sumps and not others. *E. coli* was generally highest around animal product, sanitary equipment, or in two sumps that had clearly been neglected and inappropriately used over time. Petroleum hydrocarbons were generally low in all sampled sumps, except for two sumps where point-source pollution from hydrocarbon discharges were evident (two automotive-related industries). In sumps two and four, TPH concentrations were 25,000 mg/L and 950 mg/L respectively. These concentrations are far in excess of Christchurch City Councils' 30 mg/L trade waste sewer limit for petroleum hydrocarbons, and confirm point-source pollution at these two sites. Additionally, COD was high or highest in sumps where there were both high concentrations of hydrocarbons or phosphorous/nutrients (i.e. oxygen-demanding contaminants). It should also be noted that individual business behaviour (and not just industry style) was a large factor in the contaminant concentrations found in sampled sumps.

Table 4.8 Contaminant rankings across sampled sumps and industries

Sump	Contaminant[5]													Nature of operation
	TSS	NH4-N	NNN	TN	DRP	TP	COD	*E. coli*	TPH	Cu	Zn	Pb	Cd	
1	H	H	M	H	H	H	L	H	L	H	H	M	M	Animal material processing
2	VH	H	M	H	M	H	VH	H	VH	VH	VH	VH	VH	Hydraulic servicing
3	H	H	M	H	M	M	L	H	L	H	H	H	L	Sanitary equipment cleaning
4	H	M	M	H	M	M	M	H	VH	H	H	H	M	Truck parts/repairs
5	n/a	H	M	H	H	H	M	L	L	H	H	H	M	Excavator/van depot
6	H	H	M	H	M	H	M	L	L	H	H	H	H	Bus repairs
7	H	L	M	H	M	H	M	L	L	H	H	H	L	Machinery repairs
8	L	H	M	H	M	M	L	L	L	M	H	H	L	Chemical manufacturing
9	H	H	M	H	M	H	M	L	L	H	H	M	L	Panel beating/car repairs

[5] VH, H, M, L = Very High, High, Medium and Low contamination relative to guidelines and other sampled sumps

4.4 Discussion

Loggers

Water level

This study adapted a method for the identification of dry weather discharges through the stormwater network that had proven successful in previous investigations in the same catchment (Moores et al., 2009; O'Sullivan and Charters, 2013). In this study, water level loggers were able to accurately record fluctuations in water level independent of any rainfall in the catchment, suggesting that discharges of varying volume from nearby industry were entering the stream (and thus recorded by the logger). This study, four years on from previous logging at Gerald Connolly Place by O'Sullivan and Charters (2013), has corroborated the occurrences of baseflow water fluctuations, presenting evidence that dry weather pollution and inappropriate use of the stormwater network from industries in this catchment are still ongoing.

The two main locations where discharges were consistently observed were Washbournes Road and Waterloo Road. The discharges at Washbournes Road were likely directly sourced from the large stormwater pipe the loggers were immediately put after, which was seen discharging in dry weather (and sampled-Chapter Three) several times. There were several other stormwater pipes which drain to the stream just upstream, which may have also been occasionally responsible. This confirms that the fluctuations recorded by the logger were not from random instrument error, but were accurate measurements of fluctuating water level from pipe discharges in dry weather.

The location of highest concern for the occurrence and frequency of discharges in this catchment appears to be at Waterloo Road, where the stream immediately exits the stormwater network. The loggers placed at this location indicate the very regular (almost daily) occurrence of discharges in dry weather that result in appreciable fluctuations (~25-50 mm) in stream water level. The same occurrences were identified via logging in the lower catchment in 2009, where Moores et al. (2009) found dry weather fluctuations that were above what was expected through any instrument error. O'Sullivan and Charters' (2013) investigative logging at Gerald Connolly Place found similar incidences of dry weather fluctuations, however their attempts to trace the source of fluctuations resulted in almost all discharges being sourced above the Waterloo Road stormwater network, before Haytons Stream is in open channel flow. This study has confirmed that is the case for this catchment; with logging at Waterloo Road revealing very regular discharges of varying volume and composition to the stream via the stormwater network. Further corroboration occurred when loggers were set up at GCP on 8/7/17. Logging in this location picked up the same fluctuations in dry weather reported in 2013, yet when these fluctuations were compared to those at the upstream site at Waterloo Road, they appear to be the same size and time,

and are therefore likely of same origin (i.e. the fluctuating water level at GCP is predominantly sourced from the discharges exiting the Waterloo Road stormwater pipe).

As discussed in Chapter Three, site visits to download loggers/ conduct baseflow sampling at Waterloo Road often coincided with dry weather hydrocarbon slicks exiting the stormwater network into Haytons Stream at Waterloo Road. These observed discharge signatures confirm the ability of the logger to accurately record additional inputs through the stormwater network in dry weather (i.e. record the occurrence of discharges) via continuous logging of water level.

Further, when comparing the upper catchment's loggers (comparing the logger in the manhole on Waterloo Road to the logger in Haytons Stream) interesting implications for discharge sources appear. The fluctuations observed passing through the manhole occur much more frequently yet are of a lower magnitude than those recorded in Haytons Stream. This suggests that although the frequent fluctuations in water level through the manhole are partially responsible for fluctuations seen in Haytons Stream, there must be additional dry weather inputs through the stormwater network to account for these differences in discharge magnitudes, either above or below the manhole recording location on Waterloo Road.

These upper catchment loggers have important implications for pollution prevention in this industrial catchment, presenting continual evidence over a four month period that discharges sourced through the stormwater network are still occurring at the same location since last found in 2013, and are occurring on a regular basis. Due to the hydrocarbon slicks and discharge signatures exiting the pipe on Waterloo Road, and the TPH compositions generally matching a heavy motor oil/ lubricant source, these discharges may be from the washing down of equipment/ machinery into stormwater drains from automotive industries nearby. High occurrences of automotive-style industries (such as repair shops, body or part stores) discharging wastes to stormwater networks have been found elsewhere (as well as witnessed in the field in this study), highlighting the potentially polluting nature of such operations (Schmidt and Spencer, 1986). An increased industrial pollution prevention presence is therefore likely to be most efficient in the upper catchment above Waterloo Road, where there is dense industrial land, an abundance of automotive based industries, and perhaps fewer environmentally-aware businesses.

Conductivity

Water level loggers have picked up the occurrence of illicit dry weather entries into the stormwater network, yet logging conductivity has revealed a different form of pollution to Haytons Stream, being a more diffuse ion-rich pollution in the middle catchment near Washbournes Road. At most logging locations, instream conductivity was stationary during small-moderate intensity rainfall in the catchment. This has been confirmed by both this study and previous Haytons Stream investigations, where instream conductivity values are generally lower or similar in stormflow compared to baseflow, as rainfall holds lower portions of dissolved ions than stream water during baseflow (Moores et al.,

2009; O'Sullivan and Charters, 2013). However, at Washbournes Road, evidence of 'diffuse' ion-rich pollution was consistently found in this study. The conductivity logger at this location recorded consistent spikes in instream conductivity with small amounts of rainfall in the catchment, which is corroborated with the fact that Washbournes Road was a site which generally had a higher instream conductivity during stormflow sampling runs compared to baseflow, and highly elevated instream nutrient concentrations (Chapter Three). Further, Moores et al. (2009) continuously logged at Hayton Road, downstream of this point in the catchment, and found similar occurrences of spikes in conductivity with rainfall.

Elevated nutrient and ammonia concentrations can accumulate in stormwater infrastructure in dry weather and flush out with rainfall (Memon and Butler, 2002), with a similar phenomenon recently been found in the bed sediment of Haytons Stream (Silveira et al., 2016). However, Washbournes Road is where Haytons Stream re-emerges from the reticulated stormwater network, comprising concrete piping with little room for mass organic material accumulation. Further, wet weather sampling at WBR from Chapter Three has shown large spikes in DRP, ammoniacal-N and cadmium, whereas other sites that have a higher density of industrial site/ roadside sumps closer to the stream (e.g. WAR or GCP) did not show the same wet weather spikes in such contaminants nor conductivity. This suggests that the spikes in conductivity at Washbournes Road are not just from the natural degradation and release of nitrogen from organic matter, with the actual sources of nutrient pollution and conductivity spikes in the middle catchment via the stormwater network requiring further investigation. Moores et al. (2009) found some of the highest levels of DRP in the catchment within the stormwater network at Symes Road (just upstream of this study's WBR sampling point), whereas the production of phosphate fertiliser close by on Main South Road has been stated as a large contributor to phosphorous, ammonia and nitrogen concentrations found in the lower catchment (Brown et al., 1996).

Water level and conductivity logging have successfully (and inexpensively) identified the occurrence of point and non-point source pollution to Haytons Stream. Discrete investigations within and up the reticulated stormwater network may be necessary to identify and pin-point the exact individual sources of nutrients and elevated conductivity seen in the mid catchment. Use of individual specialised sensors (e.g. ammonia, nitrate, DRP, conductivity and pH) inside the piped network may assist in determining if sources are from the same or separate locations, instead of interpreting the sources from the conductivity spikes observed in the receiving environment of Haytons Stream.

Sumps

This snapshot of industrial stormwater sumps has shown that of the sampled locations in the Haytons Stream catchment, concentrations in supernatant sump water were generally within the higher range of contaminants that have been reported (Table 4.9). Whilst nutrient and organic contaminants predominantly fell within reported ranges from past literature, metal concentrations (and therefore contamination) appear to be more severe in the Haytons catchment than reported elsewhere. Metal concentrations in this study's sumps were in the higher range of what is reported, corroborating with this study's other chapters that metal pollution, both in sediment (Chapter Two) and in the water column (Chapter Three) is a significant issue in this industrial catchment, particularly for Zn.

Table 4.9 Common pollutant concentration ranges found in stormwater sumps from other studies and this study

Parameter and reference	TSS (mg/L)	COD (mg/L)	NH_4-N (mg/L)	*E. coli* (MPN /100 ml)	Total Zn (µg/L)	Total Cd (µg/L)	Total Pb (µg/L)	Total Cu (µg/L)
(Mance and Harman, 1978)	70.7 - 1032							
(Ellis, 1986)		25 - 109		10 - 100				
(Butler and Memon, 1999)		170 - 650						
(Fletcher et al., 1978)			0.05 -9.13 (0.96 mean)					
Morrison et al. (1988)					79.4 - 406.5	4 - 13	120.5 - 192.3	277.8 - 454.5
Brown and Peake (2006)					1188 ± 194		262 ± 39	142 ± 14
This study	**4 - 2860**	**11 - 3200**	**0.01 - 2.90**	**<1 - >2420**	**221 - 35,286**	**0.13 - 37**	**6.18 - 620**	**7.67 - 989**

Only total metals were analysed in stormwater sumps, yet the concentrations indicate substantial contamination, regardless if the dissolved fraction is unknown. The metal of highest concern was again zinc, with copper also highly elevated across a number of sumps (Appendix 6 has full sump metal concentrations). Zinc and copper elevations in sumps are commonly reported, indicating their efficient release from undisturbed sump sediment into the overlying water (Morrison et al., 1988). Morrison et al. (1988) also found that between storm events, bacterial activity and acid dissolution result in increases

in total and dissolved metal concentrations within stormwater sump waters, with Zn and Cu reaching equilibrium quicker than other metal such as Pb and Cd.

Metal concentrations in this study's catchment were also substantially higher than those reported in catch basin effluents (exiting water) across the US, with mean copper and lead effluent concentrations of 3.36 and 25.6 µg/L respectively reported (Pitt and Field, 1998). These authors found little removal of metals comparing influent and effluent stormwater, highlighting the negligible treatment these structures have on metal removal from urban runoff. It is thus of small surprise that the industrial sumps sampled in the Haytons Stream catchment had significant metal concentrations in their supernatant water, which can easily transfer to the Haytons Stream water column during rainfall events, further contaminating the stream with elevated metal concentrations. This further highlights the need for greater at-source control and treatment of metals in the catchment, to avoid accumulation and transportation of elevated metals in stormwater infrastructure during both dry and wet weather.

Whilst nutrient (nitrogen and phosphorous species) concentrations in sumps were predominantly within the range of previous literature, the concentrations found still have potential to adversely impact Haytons Stream when the supernatant water is ultimately flushed out, and contribute to the poorer quality of first-flush stormwater despite the small reservoir of surface water (Butler et al., 1995). Sump liquors have been estimated elsewhere to be responsible for 11 % suspended solids, 21 % dissolved solids, 21 % COD, 16% nitrate and 32% ammonia in runoff (Fletcher and Pratt, 1981). Even considering these percentages, the sump concentrations in this study would generate a poor quality runoff to Haytons Stream in a rainfall event that flushes out the sampled sumps.

Both TN and TP were substantially above ANZECC trigger values (not accounting for dilution from rainfall or instream receiving water). Sources of nutrients (particularly ammonia) to stormwater systems can come from organic matter (such as leaf and vegetation) breakdown, which generally occurs in dry weather conditions succeeding a storm event (Butler et al., 1995; Memon and Butler, 2002). However, many of the sites visited in this catchment had limited nearby vegetation or organic material sources due to the dense industrial land use. This suggests that there may be additional sources of nutrients to these sumps, potentially such as the use and disposal of cleaning products and/ or detergents into the stormwater network. Furthermore, many visited sites in this catchment had cleaning equipment and products on site, yet did not have a dedicated wash bay that drains to the sewer network for trade waste treatment. Another source of nutrients could be from the release of the deposited sump sediment. Benthic releases of ammonia to the overlying water have been found at 32% of total ammonia present at 13 ºC, and up to 66% at warmer temperatures of 20 ºC (Memon and Butler, 2002). This occurrence has been found within the Haytons catchment, where sediment from Haytons Stream has shown increased ammonia releases through time after collection (Silveira et al., 2016), indicating sediments

can continually release ammonia within stormwater infrastructure and the stream water column during dry periods.

Concentrations of several contaminants across the sampled sumps exceed reported typical Event Mean Concentrations (EMC) for contaminants in stormwater across New Zealand catchments (Williamson, 1993). Reported 'high' EMCs across New Zealand catchments are approximately 0.25 mg/L ammonia, 0.07 mg/L DRP and 1.12 mg/L TP (Williamson, 1993). Again, whilst incoming stormwater/stream dilution was not accounted for when considering these sump water concentrations, many sumps (particularly for ammoniacal-nitrogen, and occasionally DRP and TP) are elevated far above these values, and will likely contribute to the pollution of Haytons Stream via the stormwater network in the next sufficient rain event. Previous investigations of stormwater runoff in the lower Haytons catchment found substantially elevated contaminants beyond the suggested ranges from Williamson (1993), corroborating that the Haytons Stream catchment generates stormwater runoff with elevated and environmentally relevant contaminant concentrations (Brown et al., 1996).

Given that prolonged dry periods with temperatures at 20 ºC or above generate poorer sump water quality (Memon and Butler, 2002), it is recommended that sump water concentrations be re-surveyed, across a wider number of businesses and industries, during summer months when there are significant dry periods. This will allow a greater quantification of the 'worst-case' of potential contaminants generated within and from stormwater sumps in the industrial catchment, which could then be transferred into Haytons Stream.

From this one-off sump snapshot, the selected sumps contained highly elevated concentrations of metals (particularly Zn in all, and occasionally Cu, Pb and Cd). Nutrient concentrations predominantly fell within reported concentrations in sump water, yet the individual sources and nature of visited sites in this highly impervious catchment indicate that there may be a more anthropogenic and pollution-based origin rather than the breakdown of organic matter that has been found elsewhere (Memon and Butler, 2002; Butler et al., 1995). Dissolved metal content should be surveyed across sumps in the catchment, as the elevated concentrations of total metals suggest that there may be highly elevated concentrations of dissolved fractions in these sumps, given that sumps have been shown to increase the ratio of particulate/ sediment-bound metals into more dissolved/ bioavailable forms during dry weather (Morrison et al., 1988).

4.5 Conclusions

Continuous logging of water level and conductivity was successful in the identifying of dry and wet weather pollution in the catchment. Two locations (Washbournes Road in the middle catchment and Waterloo Road in the upper catchment) consistently had fluctuations in water level in dry weather indicating discharges from industry via the stormwater network. Waterloo Road had frequent 'dry-weather discharges' exiting the stormwater pipe into the stream, occurring on an almost daily basis over the four month logging period. When discharges were observed at this location in the field, they were frequently associated with hydrocarbon slicks/ signatures exiting the network, corroborating the loggers' ability to record these dry weather discharges. Conductivity logging revealed that pollution in the mid catchment is likely from ion-rich stormwater, seen through large instream conductivity spikes at WBR that were not seen elsewhere in Haytons Stream during small to moderate intensity rainfall events. The individual sources of high conductivity and nutrient concentrations seen at WBR in Chapter Three need to be tracked to mitigate nutrient pollution in the mid catchment. This could be potentially investigated via tracing/ logging of specific parameters through the stormwater network to an individual source(s). Industrial pollution prevention efforts would therefore be more efficient by targeting hydrocarbon/ automotive-related industries in the upper catchment, and potential nutrient/ chemical-related industries in the mid catchment for increased stormwater education, management and site audits.

The results of a snapshot sampling campaign of industrial sumps in the Haytons Stream catchment revealed that most sumps contained elevated concentrations of trace elements and nutrients in overlying sump water. Nutrient concentrations were generally in line with reported literature (although sources may be anthropogenic as well as natural), yet trace element concentrations (particularly Zn and Cu) were above what has been found elsewhere, further confirming the substantial metal pollution issue this industrial catchment has, as shown in the previous two chapters in water and sediment.

Chapter 5 Overall research conclusions

Synthesis of findings

This study has corroborated with the vast body of literature on urban stream water quality and the negative effects that urbanisation and impervious surface coverage can have on waterways. Haytons Stream in industrial south-west Christchurch has been no exception, as it displays many of the characteristics typical of a degraded urban waterway, including; elevated trace elements, nutrients, suspended sediments and a reduced to non-existent ecological presence (Paul and Meyer, 2001; Walsh et al., 2005).

The overall aim of this research was to increase the understanding and identification of contaminants within and discharged to Haytons Stream, and to increase the understanding of the mechanisms for how contaminants are sourced to the waterway. Separate individual objectives to do this involved sediment, baseflow, stormflow and industrial sump sampling, plus continuous logging of water level and conductivity trends across the catchment to identify evidence of dry weather inputs to the stream. The results of this research have shown that there are numerous sources of contaminants to Haytons Stream, including point-sources from industrial discharges (predominantly hydrocarbon-based in the upper catchment and nutrient-based in the middle catchment) and non-point sources from the industrial catchment, which amalgamate to create the poor baseflow and stormflow water quality the stream has become known for.

Stream bed sediment

The <2 mm fraction of sediment along Haytons Stream was analysed for pseudo-total and bioavailable/ labile metal content (using a weak acid extraction). Pseudo-total metal concentrations were elevated at several sites for Ni, Cu, Cd and Pb, whilst Zn concentrations were highly elevated throughout the whole catchment, with concentrations suggesting severe zinc contamination. Bioavailable fractions of metals (representing metals weakly bound to sediment matrices, or in a 'labile' state), remained highly elevated for Zn across the stream, indicating there are substantial sources of metals within the bed sediment that can be re-released to the water column. Total Phosphorous and cadmium concentrations in sediment spiked dramatically at Washbournes Rd, indicating a particular source of these contaminants in the mid catchment. Sediment concentrations in this study were far above those found in other Christchurch catchments thought to hamper and degrade ecological diversity, with sediment quality likely one of the main drivers of the very poor to non-existent aquatic ecosystem seen throughout Haytons Stream (McMurtie, 2002).

Remediation of sediment throughout the stream may be required, for both any future ecosystem considerations and the implication that the bed sediment is potentially a continual source of metals to

the water column. Tangible water quality and ecological improvements will likely be continually limited if the contaminated sediment is left as is. Furthermore, Haytons Stream was re-aligned and a new substrate of fresh river gravel was created just five years ago. The current substrate at these re-aligned sites is now dominated with thick, anoxic-smelling fine sediment/ silts, harbouring the elevated concentrations of metals found in this study. This indicates that metal pollution is occurring on a continual and rapid scale, as this fine sediment is under five years old yet already substantially contaminated. This highlights that not only remediation, but greater at-source metal treatment in the industrial sections of the catchment are required to remove legacy effects of historical sediment, and mitigate the continual pollution of metals that is clearly occurring.

Instream sampling and monitoring

The sampling of three baseflow and three stormflow events has revealed that trace elements are elevated in the water column of Haytons Stream at all times (during dry and wet weather), where concentrations of Al, Zn, Cu and Cd reached orders of magnitude higher than their respective guideline values for 80% species protection. Several metal concentrations were significantly higher in the upper (industrial) catchment sites compared to the lower (pastoral/ re-landscaped) catchment sites, indicating the industrial land use in the upper catchment is a significant source of metals to Haytons Stream. There are abundant sources of metals found in industrial urban environments (Kennedy and Sutherland, 2008), all of which are also present in the Haytons Stream catchment. Elevated dissolved metal concentrations during baseflow correlated well with labile bed sediment concentrations across the catchment, suggesting that the bed sediment is a source of these dissolved metals to the stream during baseflow.

The effectiveness of the Wigram Retention Basin was a concern in this study, with net exports of most analysed metals seen out of the basin during baseflow, whilst exiting stormflow concentrations remained elevated. This has highlighted that the wetland is very poor in removing metal concentrations in the water column during dry weather, leading to the significant effect Haytons Stream has on the Heathcote River's downstream metal concentrations (particularly for Zn, Cu and Al). The quality of sediment within the basin itself may be a concern for metal release, given the labile concentrations of metals within Haytons Stream, which eventually discharges into the basin in the lower catchment. Upgrades to the efficiency of the basin, particularly in removing total and dissolved metal contaminants, plus greater adoption of at-source treatment of metals in the upper catchment is likely necessary if reduced concentrations are to be seen instream (and subsequently in sediment) in both Haytons Stream and the downstream Heathcote River.

Instream nutrient (ammoniacal-nitrogen and dissolved reactive phosphorous) concentrations spiked in both dry and wet weather at the mid catchment site of Washbournes Road. Highly elevated concentrations of up to 4 mg/L DRP and 13.5 mg/L ammoniacal-N were found during stormflow conditions at WBR, indicating stormwater runoff is a major conveyer of nutrients to Haytons Stream,

and a substantial source of nutrients exists somewhere in the mid catchment near Washbournes Road, which is not causing such elevated concentrations in the upper or lower catchment. This mid catchment nutrient spike has been reported across other studies over the past 20 years (Brown et al., 1996; Moores et al., 2009; Silveira et al., 2016), indicating the same source(s) have continued to have poor site and stormwater management over this time. When combining these nutrient concentrations with continuous logging, there is a clear case for wet weather nutrient pollution in the mid catchment. Conductivity logging has shown that Haytons Stream at Washbournes Road tended to spike in conductivity during small to moderate intensity rainfall events (~0.2 mm/10 minutes), whilst other locations across the catchment tended to have diluted/ stationary conductivity trends in similar intensity events. These conductivity spikes at Washbournes Road, matched with elevated DRP and ammoniacal-N during stormflow sampling, corroborate that there is a large source of nutrients (high-ion/nutrient-contaminated stormwater) to Haytons Stream in the middle catchment, close to Washbournes Road upstream in the stormwater network.

This study has displayed the successful use of inexpensive water level loggers to identify industrial discharges to waterways in dry weather, represented through fluctuations (rises) in water level in absence of rainfall. Loggers recorded discharges in the middle (Washbournes Road) and upper catchment (Waterloo Road); both sourced and entering the stream via the reticulated stormwater network. The majority of observed discharges in the upper catchment were sourced from the stormwater network above open channel flow in Haytons Stream, restricting the ability for discharges to be tracked back to individual sites. When discharges were observed in the field exiting the piped network at Waterloo Road, they were often associated with hydrocarbon-style slicks on the stream surface, suggesting automotive or similar-style industries are commonly contributing to the illicit use of the stormwater network. Therefore, pollution prevention efforts should delineate from the middle catchment, and focus on increased education and stormwater audits for automotive-based or similar industries in the upper catchment, to avoid inappropriate dry weather entries into storm drains and Haytons Stream in this industrial land. In the middle catchment, pollution prevention efforts should target industries known for high nutrient use or production in their operations, to avoid further stormwater contamination and pollution of Haytons Stream near Washbournes Road.

Stormwater sumps

Industrial sites in the catchment were targeted for sump sampling based on the perceived ‘risk’ of discharges. Of the sites visited, trace element pollution was evident and widespread across all sumps, with highly elevated concentrations of total metals (particularly Zn and Cu) found. This corroborates back with water column sampling in this thesis, validating that the dense industrial land use in the upper catchment is a significant source of metal pollution to the stream. Nutrient concentrations within sumps were within the general range for what has been reported globally, yet the sources (i.e. organic matter

breakdown or anthropogenic) remain unclear. Given the presence of cleaning products and equipment at numerous visited sites without a designated wash bay to sewer, it is recommended further stormwater education and audits take place throughout the catchment to limit the disposal of any inappropriate industrial product into stormwater sumps, eventually discharging to (and polluting) Haytons Stream.

Future research

This thesis has highlighted the key areas within the Haytons Stream catchment which need to be targeted for pollution mitigation, for long-term water quality improvements. If bed sediment is not/ cannot be remediated or removed, further quantification of individual metal bioavailability and re-release to the water column within sediment in Haytons Stream is required.

Further research into the specific source of the mid catchment nutrient spike reported in this study and others is needed, given the highly elevated concentrations of ammoniacal-N and DRP found at Washbournes Road. Individual parameter sensors, such as those adopted by Moores et al. (2009), installed within the reticulated stormwater network may help to delineate where these high-concentration pulses are sourced from, and to determine if there are additional sources on top of that stated by Brown et al. (1996), which can then be targeted for further pollution prevention to prevent the ongoing nutrient pollution of Haytons Stream.

Further/ continued monitoring of industrial site sumps is recommended to gain a greater understanding of pollutants potentially discharged to Haytons Stream, particularly during long dry weather periods in summer months when sump water quality is generally worse, and including dissolved metal fractions.

Further research is needed to understand the processes of absorption and release of metals/ nutrients from river bed sediment, as well as to holistically understand contaminant transport processes along Haytons or any other stream. Research into real-time monitoring and in-situ alert systems would also further assist in point-source pollution identification and reduction, for example if real-time alerts can be sent out (and users notified) if there are dry weather fluctuations or evidence of discharges occurring in a stream. Additional beneficial research is also not necessarily limited to this small sub-catchment, and could extend to a similar study on the neighbouring Curletts Stream, which has been shown to have similar concentrations of contaminants (Margetts and Marshall, 2016; Marshall and Burrell, 2017), with similar negative impacts on the Heathcote River. Increased knowledge of contaminants and their sources in this neighbouring industrial catchment will further assist and benefit pollution prevention efforts, as well as further benefit the protection of the downstream Heathcote River/ Ōpāwaho.

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Appendix 1- Sampling sites for sediment and water in this study

Waterloo Road

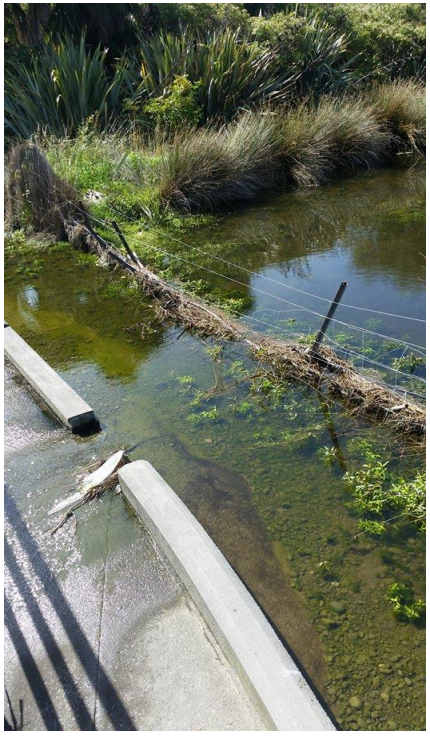
Gerald Connolly Place

Washbournes Road

Lodestar Avenue

The Runway

Wigram Road



Upstream of the Wigram Retention Basin

Downstream of the Wigram Retention Basin

Heathcote River above Haytons Stream

Heathcote River below Haytons Stream

Appendix 2- Pseudo-total and bioavailable trace element concentrations in sediment throughout Haytons Stream

Pseudo-total trace elements in Haytons Stream sediment

Elements	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
ANZECC ISQG-low						80				21	65	200	20		1.5	2	50
ANZECC ISQG-high						370				52	270	410	70		10	25	220
Sites																	
WAR	4228	14700	8291	1076	32.9	57.5	249	19815	10.4	23.7	149	3455	10.5	5.65	1.16	2.54	184
GCP	5111	16527	12606	1193	36.7	64.0	295	22978	9.61	26.6	144	3466	11.5	5.86	1.48	3.28	121
WBR 1	3192	9721	49255	720	24.9	35.9	226	14798	5.98	13.2	54.9	877	4.49	1.32	6.16	0.61	79.7
WBR 2	3007	11309	63261	775	27.4	40.5	170	12726	6.05	17.9	33.9	2245	5.33	2.35	8.28	0.55	115
LSA	3643	12408	12737	1158	26.2	49.4	210	16599	7.35	16.6	68.9	2568	9.20	2.12	1.90	1.71	121
TRW	5852	21048	12131	1379	38.3	54.2	313	25940	12.7	21.3	96.9	2976	12.2	2.69	1.90	1.59	126
WGR	3940	11400	5328	1176	21.8	27.2	220	16167	6.71	14.9	44.0	978	6.64	1.41	0.39	0.58	48.9
UWB	4377	16027	7988	1038	29.2	33.8	208	17217	7.63	15.7	59.6	1839	6.63	1.37	1.72	0.62	120
DWB	3004	7346	3558	828	15.4	10.0	199	11614	5.54	7.94	5.95	218	2.46	0.20	0.18	0.07	8.99
HEA-UHS	3146	9890	8683	914	24.1	20.3	173	15646	8.27	10.8	30.2	351	9.64	0.55	0.86	0.27	83.4
HEA-DHS	2982	9088	5077	933	19.7	16.1	192	13956	7.73	9.69	19.4	1032	5.82	0.42	0.81	0.26	42.2

Bioavailable trace elements in Haytons Stream sediment

Elements	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
ANZECC ISQG-low						80				21	65	200	20		1.5	2	50
ANZECC ISQG-high						370				52	270	410	70		10	25	220
Sites																	
WAR	862	4025	4206	105	9.83	29.1	70.4	5859	4.31	12.3	92.3	3850	3.68	0.19	0.96	0.30	146
GCP	1024	4581	6944	101	9.18	33.4	83.5	7032	3.65	13.2	81.6	3685	3.51	0.19	1.25	0.00	96.9
WBR 1	1359	3223	44480	112	9.37	15.7	135	5986	2.25	5.58	22.0	1327	2.23	0.43	9.98	0.00	47.8
WBR 2	1335	2850	41046	110	10.7	16.8	73.8	4012	1.32	5.42	13.2	2229	2.49	0.18	5.73	0.00	127
LSA	661	3128	7483	91.3	5.95	19.3	53.6	4880	2.79	6.44	39.0	2879	4.06	0.00	1.66	0.00	100
TRW	1251	6208	8043	155	10.4	22.2	108	8705	5.75	8.09	78.7	3822	5.50	0.05	2.04	0.00	126
WGR	464	2452	2372	82.3	3.64	11.4	41.6	3445	2.14	5.99	28.8	1113	3.23	0.00	0.38	0.00	39.5
UWB	445	3048	4262	88.0	5.83	6.45	35.5	2919	1.71	3.83	29.8	1846	3.05	0.00	0.19	0.00	107
DWB	269	1042	1298	22.2	2.01	2.27	43.7	1997	1.29	1.36	4.67	218	1.18	0.00	0.19	0.00	8.32
HEA-UHS	498	2074	4282	87.3	7.11	3.16	37.9	3383	2.83	3.09	15.6	238	4.32	0.00	0.72	0.00	57.8
HEA-DHS	331	1708	2166	54.7	4.27	5.51	46.6	3422	2.86	2.55	12.2	1010	5.09	0.00	0.79	0.00	34.3

Appendix 3- Copy of returned Chain of Custody (COC) form submitted to Hill Laboratories for sample analysis

Hill Laboratories
TRIED, TESTED AND TRUSTED

ANALYSIS REQUEST

R J Hill Laboratories Limited
1 Clyde Street Hamilton 3216
Private Bag 3205
Hamilton 3240 New Zealand

T 0508 HILL LAB (44 555 2
T +64 7 858 2000
E mail@hill-labs.co.nz
W www.hill-laboratories.com

Job No: **178 3421**
Date Recv: 29-May-17 13:39
Received by: Natalia Leatua
3117834218

Quote No 84395

Primary Contact Lewis Black 234517

Submitted By Lewis Black 234517

Client Name Environment Canterbury - Surface Water 184365

Address C/- Environment Canterbury, PO Box 345
Christchurch 8140 *Postcode*

Phone *Mobile*

Email surfacewatersampling@ecan.govt.nz

Charge To Environment Canterbury 32659

Client Reference P026900 MSc project

Additional Client Ref SWINV

Order No 69079

Results To *Reports will be emailed to Primary Contact by default. Additional Reports will be sent as specified below.*

☑ Email Primary Contact ☐ Email Submitter ☐ Email Client
☑ Email Other lewis.black@pg.canterbury.ac.nz
☐ Other

ADDITIONAL INFORMATION

CHAIN OF CUSTODY RECORD

Sent to Hill Laboratories
☑ Tick if you require COC to be emailed back
Date & Time: 29/5 1:35pm
Name: Lewis Black
Signature: Lewis Black

Received at Hill Laboratories
Date & Time:
Name: NAE
Signature:

Condition ☐ Room Temp ☐ Chilled ☐ Frozen Temp: 8

☐ Sample & Analysis details checked
Signature:

Priority ☐ Low ☑ Normal ☐ High
☐ **Urgent** (ASAP, extra charge applies, please contact lab first)

NOTE: The estimated turnaround time for the types and number of samples and analyses specified on this quote is by 4:30 pm, 5 working days following the day of receipt of the samples at the laboratory.

Requested Reporting Date:

Quoted Sample Types
Surface Water (SW)

No.	Sample Name	Sample Date/Time	Sample Type	Tests Required
1	SQ36042 - Haytons Stream at Waterloo Rd	09.45/29/5	SW	ECmpnQTchch, NH4NchH, NOxNchH, DRPchH
2	SQ30572 - Haytons Stream at Washbournes Rd	10.40 29/5	SW	ECmpnQTchch, NH4NchH, NOxNchH, DRPchH
3	SQ36266 - Haytons Stream above Wigram Retention Basin	12.20 29/5	SW	ECmpnQTchch, NH4NchH, NOxNchH, DRPchH
4				
5				
6				
7				
8				
9				
10				

Appendix 4- Total and dissolved trace elements across all Haytons Stream sampling runs, duplicate results and HMTV calculations

Baseflow (BF):

Totals (µg/L)	BF1	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		1389	304	21583	10.9	2.61	1.17	37.2	240	1.88	0.76	2.38	114	1.23	1.88	0.04	1.02	1.46
GCP		1412	244	16612	14.2	1.02	0.97	89.6	1432	2.10	1.04	3.61	119	1.08	1.42	0.04	0.62	1.51
WBR		2138	585	19550	29	2.22	1.85	191	1141	3.23	1.93	6.9	276	2.01	2.08	0.15	0.84	3.16
LSA		1225	428	11878	21.4	0.93	0.67	19.2	326	1.74	0.48	5.00	104	1.12	1.01	0.18	0.71	1.71
TRW		1171	387	10142	16.9	1.11	0.68	25.3	380	1.72	0.83	2.76	185	1.53	1.30	0.03	0.53	1.48
WGR		1727	528	14952	27.9	1.20	1.07	33.2	528	1.76	0.86	2.47	102	1.66	1.09	0.04	0.92	1.66
UWB		2812	292	14165	14.1	1.15	0.86	8.07	228	1.45	0.83	2.41	78.8	1.65	1.46	0.02	0.65	1.17
DWB		1719	545	9399	27.8	1.42	3.04	32.0	534	1.62	0.96	3.78	189	1.92	1.80	0.17	0.81	2.19
HEA-UHS		6196	49.7	34364	1.98	0.14	0.28	15.0	67.3	1.48	0.35	0.39	7.29	0.43	0.83	0.00	2.08	0.23
HEA-DHS		5682	118	30845	5.26	0.48	22.7	16.3	127	1.48	0.54	1.08	41.6	0.70	0.96	0.01	1.35	0.63

Dissolved (µg/L)	BF1	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		1256	19.0	20270	1.48	1.95	0.71	33.0	24.7	1.36	0.46	1.23	100	1.29	1.89	0.03	1.74	0.34
GCP		1442	17.4	18076	1.37	0.62	0.37	93.6	760	1.84	0.87	1.04	76.0	1.23	1.77	0.02	1.17	0.52
WBR		2009	106	19858	1.78	1.89	1.01	188.6	474	2.84	1.50	2.88	229	1.82	2.17	0.05	1.18	0.73
LSA		963	29.9	9788	1.40	0.49	0.00	13.7	45.5	1.25	0.41	1.18	76.3	1.01	1.18	0.01	0.63	0.33
TRW		995	24.5	9227	2.37	0.49	0.25	20.2	79.5	1.30	0.51	1.69	170	1.44	0.82	0.01	0.96	0.37
WGR		1406	29.5	12962	0.63	0.38	0.31	23.0	70.6	1.25	0.45	1.34	90.3	1.15	1.28	0.02	0.60	0.37
UWB		2323	30.1	12043	1.42	0.55	0.08	5.04	32.0	1.21	0.57	1.78	64.7	1.48	0.99	0.04	0.50	0.30
DWB		1498	21.9	8654	1.04	0.60	0.31	3.80	25.3	1.14	0.54	2.29	147	1.62	1.47	0.06	0.86	0.23
HEA-UHS		5414	8.38	29522	0.82	0.14	0.00	13.3	23.3	1.18	0.29	0.16	8.09	0.38	0.56	0.02	0.43	0.10
HEA-DHS		4481	11.7	24446	2.01	0.24	0.09	10.8	21.3	1.11	0.40	0.42	34.1	0.46	0.54	0.00	0.34	0.16

Totals (µg/L)	BF2	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		1927	1949	23665	102	4.39	2.88	104	2249	2.55	2.31	10.8	187	2.61	2.88	0.05	0.87	6.81
GCP		1797	146	21578	5.71	0.89	1.16	126	2411	2.78	1.43	2.85	101	1.47	1.66	0.62	0.68	1.50
WBR		2302	390	23931	17.2	1.88	4.16	236	1714	3.63	2.25	7.75	1242	2.17	2.03	2.25	0.87	11.3
LSA		1182	373	11621	23.0	1.01	0.77	23.8	363	1.65	0.60	2.44	98.2	1.15	0.83	0.04	0.51	1.92
TRW		1261	282	11485	8.55	0.86	0.44	30.5	402	1.66	0.81	2.76	164	1.51	1.22	0.05	0.44	1.54
WGR		1543	387	13324	15.2	1.10	17.7	19.4	437	1.55	0.64	2.94	75.8	1.45	1.22	0.05	0.48	1.64
UWB		3330	206	16656	8.10	0.81	0.49	8.30	179	1.42	0.66	2.18	69.5	1.26	0.90	0.01	0.51	0.75
DWB		1963	542	10050	32.2	1.45	0.94	34.1	554	1.66	1.06	3.77	177	1.75	1.21	0.81	0.85	2.33
HEA-UHS		6044	80.3	32897	3.48	0.23	0.51	13.9	85.5	1.57	0.50	1.15	9.54	0.37	0.70	1.09	2.35	0.33
HEA-DHS		5340	134	28896	6.51	0.43	0.26	17.5	161	1.47	0.53	1.40	42.9	0.65	0.62	7.28	1.44	0.55

Dissolved (µg/L)	BF2	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		1380	21.5	20093	1.35	1.33	0.45	71.7	149	1.69	0.95	2.48	84.7	1.98	2.33	0.00	0.85	0.82
GCP		1637	17.3	19619	1.67	0.67	0.41	116	1587	2.22	1.19	0.97	51.9	1.19	1.54	0.02	0.44	0.60
WBR		1905	67.5	19951	1.50	1.01	0.56	194	409	2.80	1.45	2.05	186	1.34	2.16	0.01	0.61	0.54
LSA		946	25.8	9710	0.78	0.48	0.11	17.4	69.3	1.30	0.60	0.96	64.6	0.94	0.88	0.00	0.43	0.37
TRW		1158	28.6	10785	1.32	0.62	0.16	26.7	116	1.28	0.62	1.73	147	1.29	1.09	0.03	0.53	0.43
WGR		1355	58.5	12130	2.64	0.54	0.24	14.2	95.6	1.15	0.39	1.75	44.0	1.39	0.99	0.00	0.59	0.46
UWB		2719	21.5	13504	0.77	0.54	0.19	5.30	25.7	1.19	0.53	1.32	57.1	1.18	0.89	0.02	0.36	0.23
DWB		1714	33.6	9187	2.24	0.79	0.42	3.06	28.8	1.13	0.58	2.39	67.1	1.49	1.18	0.01	0.44	0.23
HEA-UHS		6066	8.88	32478	0.78	0.10	0.03	13.1	22.2	1.21	0.36	0.24	6.39	0.27	0.48	0.00	0.38	0.13
HEA-DHS		4822	9.12	25876	0.78	0.26	0.04	12.0	20.3	1.17	0.34	0.47	33.1	0.55	0.55	0.01	0.29	0.13

Totals (µg/L)	BF3	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		1308	398	24984	14.4	3.25	2.91	57.5	423	0.79	0.82	4.38	121	1.36	19.9	0.03	1.60	2.33
GCP		1561	291	24024	14.3	1.32	1.76	117	1891	1.67	1.65	4.49	137	1.51	22.6	0.05	1.22	2.69
WBR		1425	477	21373	27.9	1.67	1.76	78.8	1237	1.07	2.07	4.65	152	3.13	21.1	0.04	1.85	1.69
LSA		1174	820	12650	31.9	1.86	14.68	61.7	1681	0.82	1.29	3.98	107	2.04	20.2	0.06	1.57	4.53
TRW		1349	554	12289	22.7	1.58	1.06	48.5	912	0.67	1.03	3.31	130	2.25	19.8	0.03	1.42	2.24
WGR		2926	262	30127	13.7	0.78	0.76	58.4	534	0.42	0.57	1.42	23.9	1.49	19.4	0.01	1.34	1.11
UWB		1638	393	12035	18.1	1.65	1.04	18.8	439	0.48	0.85	3.83	133	3.04	19.6	0.05	1.40	1.77
DWB		1516	322	9991	15.7	1.55	1.23	33.5	377	0.36	0.72	3.64	165	2.50	19.8	0.03	1.28	1.35
HEA-UHS		5877	70.3	39289	3.52	0.26	0.23	20.4	104	0.36	0.52	0.35	3.93	0.60	19.2	0.01	2.62	0.20
HEA-DHS		5264	97.5	35197	5.18	0.33	0.40	21.1	137	0.30	0.50	0.88	27.7	0.75	19.3	0.02	1.95	0.22

Dissolved (µg/L)	BF3	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		1088	23.8	20901	2.36	2.16	2.26	27.2	27.0	0.37	0.40	1.05	55.0	1.48	18.5	0.02	3.17	0.16
GCP		1419	21.2	21529	2.65	0.72	1.09	104	663	1.37	1.42	1.84	89.4	1.58	20.2	0.04	2.55	1.46
WBR		1064	24.8	16494	3.06	0.89	0.91	55.3	222	0.74	1.49	1.89	83.7	2.38	18.7	0.04	2.13	0.36
LSA		911	41.0	10808	3.13	0.45	5.14	46.8	399	0.57	0.63	1.07	46.4	1.51	17.2	0.02	1.90	0.62
TRW		1130	36.7	10567	3.18	0.79	0.47	38.2	28	0.43	0.63	1.88	107	2.00	16.7	0.02	1.92	0.67
WGR		2579	11.2	26051	2.06	0.32	0.26	47.8	67.0	0.24	0.35	0.56	13.7	1.23	17.0	0.01	1.73	0.15
UWB		1453	29.5	10798	3.77	1.19	0.31	14.6	101	0.30	0.85	2.61	118	2.89	17.2	0.02	1.83	0.44
DWB		1351	23.1	8718	2.92	0.93	0.72	0.89	31.5	0.15	0.60	2.53	91.3	2.54	16.8	0.02	1.47	0.13
HEA-UHS		5113	8.47	32355	1.90	0.20	0.00	17.3	39.4	0.27	0.33	0.28	6.41	0.49	16.1	0.02	0.92	0.10
HEA-DHS		4969	12.3	30202	2.20	0.32	0.22	18.2	36.4	0.26	0.50	0.59	26.1	0.73	16.0	0.02	0.87	0.11

Stormflow (SF):

Totals (µg/L)	SF1	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		510	1492	4516	97.2	3.09	5.02	28.0	1378	1.87	3.55	7.99	222	2.43	1.31	221	0.95	5.13
GCP		491	1403	3583	85.7	2.91	4.38	25.0	1257	1.86	1.51	6.83	199	2.37	1.59	6.08	0.99	4.00
WBR		975	1223	5709	76.9	2.98	5.00	31.4	1182	1.91	1.95	7.83	173	2.45	1.34	6.05	0.85	4.25
LSA		700	1167	8979	63.8	2.30	2.90	23.8	1012	1.76	1.59	7.01	177	1.95	1.21	0.10	1.03	4.20
TRW		572	664	3503	45.4	1.74	1.98	17.4	576	1.63	0.81	4.41	186	1.46	1.25	0.08	0.51	2.36
WGR		794	566	4317	33.5	1.72	1.97	19.7	501	1.63	1.05	5.97	210	1.54	1.05	3.44	0.80	2.33
UWB		1127	965	6111	72.9	2.16	2.07	23.4	919	1.72	2.58	6.27	248	2.11	1.23	0.23	0.80	4.29
DWB		1909	499	10194	31.1	1.37	0.79	32.7	498	1.53	0.89	3.28	107	1.78	1.24	2.92	0.51	1.94
HEA-UHS		6097	154	30977	9.09	0.30	0.51	37.6	217	1.60	0.64	0.75	15.4	1.14	1.69	0.01	7.10	0.61
HEA-DHS		3287	356	17205	20.1	1.23	0.94	34.8	412	1.75	0.95	2.60	82.8	1.66	1.30	0.33	2.41	1.56

Dissolved (µg/L)	SF1	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		183	29.4	2651	0.76	0.69	2.68	4.60	15.7	1.15	0.26	2.23	103	2.24	0.93	0.01	0.67	0.32
GCP		182	28.4	2639	1.26	0.72	2.43	4.35	19.3	1.10	0.21	2.09	102	2.03	0.99	0.00	0.63	0.21
WBR		615	29.6	3991	1.27	0.77	1.68	10.4	20.3	1.26	0.48	2.42	84.9	1.86	1.10	0.03	0.58	0.17
LSA		405	25.5	2799	0.75	0.54	0.71	7.23	18.2	1.19	0.34	2.12	113	1.42	0.82	0.03	0.36	0.21
TRW		458	25.3	3096	1.30	0.66	0.77	9.12	21.5	1.18	0.40	2.25	165	1.51	1.09	0.03	0.47	0.28
WGR		707	23.1	12230	1.33	0.74	0.93	12.5	25.6	1.22	0.49	2.65	196	1.54	1.03	0.02	0.50	0.40
UWB		829	21.0	4779	1.90	0.59	0.64	9.03	32.0	1.14	0.56	2.68	180	1.53	0.93	0.03	0.60	0.26
DWB		1704	54.1	8831	1.27	1.00	0.06	1.52	38.6	1.18	0.49	2.13	20.4	1.65	1.10	0.01	0.48	0.28
HEA-UHS		5307	19.7	26482	1.64	0.15	0.05	31.9	67.2	1.32	0.53	0.49	19.9	0.88	0.46	0.01	0.10	0.20
HEA-DHS		2800	26.7	14589	1.27	0.68	0.15	11.8	38.4	1.20	0.54	1.55	45.5	1.33	0.82	0.01	0.49	0.25

Totals (µg/L)	SF2	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		2674	8743	22021	480	13.2	13.4	131	6551	2.98	6.39	24.6	753	5.31	21.9	0.21	2.48	31.1
GCP		1728	5238	21886	133	6.18	7.24	49.7	2229	1.22	2.87	15.6	377	3.56	21.2	0.12	1.76	9.98
WBR		11471	3099	38439	186	7.40	9.07	137	3030	4.18	6.00	33.4	608	4.73	23.6	0.88	3.63	12.5
LSA		1227	1051	13870	43.4	1.87	2.18	46.9	964	1.07	1.55	6.93	553	1.90	19.4	0.08	1.57	4.52
TRW		1559	542	13338	23.8	1.57	1.72	44.8	706	0.65	1.52	4.68	339	2.42	19.5	0.06	1.57	2.36
WGR		3490	7406	25470	501	11.6	9.39	138	6394	2.61	5.46	14.6	443	4.78	19.7	0.12	1.34	17.5
UWB		2169	399	15442	20.0	1.12	1.04	15.2	330	0.48	1.06	3.67	183	1.69	19.3	0.04	0.96	1.19
DWB		1264	552	8398	31.6	1.52	1.73	25.1	518	0.34	0.97	4.09	203	2.04	19.3	0.06	0.93	1.88
HEA-UHS		5457	59.3	36580	2.89	0.27	0.24	17.0	99.2	0.27	0.51	0.47	11.4	0.32	18.7	0.01	0.59	0.46
HEA-DHS		4073	187	27382	10.0	0.65	0.56	18.7	226.8	0.33	10.2	1.65	76.2	0.89	18.9	0.03	0.73	0.74

Dissolved (µg/L)	SF2	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		945	47.0	11510	2.80	1.33	1.55	18.8	130	0.28	0.86	7.40	104	2.07	17.3	0.03	1.39	1.23
GCP		1035	35.0	14418	1.61	1.50	1.37	19.2	62.9	0.40	0.58	3.22	143	1.23	17.4	0.04	1.10	0.30
WBR		9244	25.9	26280	3.41	2.25	0.56	68.0	54.0	2.31	2.73	5.82	197	2.92	20.4	0.06	1.60	0.29
LSA		978	68.9	12021	2.24	0.83	0.44	33.3	137	0.53	0.90	2.88	474	1.36	16.4	0.03	1.02	0.85
TRW		1253	28.5	11654	2.37	0.65	0.74	33.3	143	0.41	0.83	2.67	285	1.98	16.4	0.03	1.10	0.47
WGR		1717	25.8	19754	2.89	0.52	0.74	31.6	73.4	0.32	0.72	3.08	208	1.55	16.4	0.01	0.98	0.26
UWB		2075	23.5	13733	2.66	0.81	0.40	8.36	34.5	0.24	0.68	2.12	172	1.73	16.2	0.04	0.75	0.22
DWB		1119	22.6	7856	2.15	0.78	0.50	3.56	34.6	0.14	0.53	2.57	164	2.00	16.2	0.03	0.70	0.25
HEA-UHS		5125	9.78	33864	2.28	0.22	0.29	15.0	37.1	0.21	0.51	0.35	8.12	0.32	15.6	0.01	0.66	0.06
HEA-DHS		3899	10.3	24986	1.90	0.41	0.17	14.1	35.6	0.18	0.75	0.89	63.5	0.89	16.0	0.02	0.61	0.10

Totals (µg/L)	SF3	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		801	3416	9667	46.3	3.74	5.78	22.8	787	0.65	1.76	11.0	459	3.54	20.5	0.07	1.61	3.90
GCP		702	1238	7384	40.5	2.91	3.72	21.6	664	0.59	1.37	10.4	396	2.22	20.7	0.08	1.61	2.76
WBR		1677	533	8633	20.3	2.79	4.38	27.7	442	0.68	1.55	11.5	309	2.32	21.5	0.21	1.37	1.92
LSA		1256	383	8463	20.1	1.95	2.85	26.3	520	0.65	1.34	10.8	682	2.22	20.7	0.11	1.37	2.64
TRW		2210	340	13754	18.8	2.29	2.71	37.9	520	0.74	2.20	16.3	823	3.04	21.7	0.25	1.51	2.56
WGR		2676	404	18632	30.4	2.08	4.24	44.5	769	0.69	2.31	14.1	779	3.15	21.1	0.32	1.34	2.94
UWB		2102	352	13853	25.6	1.67	1.10	23.9	563	1.05	1.32	12.9	234	2.88	22.0	0.04	1.23	2.47
DWB		1847	303	12298	14.7	1.45	0.63	69.9	556	0.56	0.78	3.16	93.8	3.79	19.5	2.19	0.80	1.78
HEA-UHS		5265	51.3	33210	2.63	0.22	0.37	18.7	95.6	0.27	0.65	0.45	6.35	0.59	20.2	0.02	7.77	0.19
HEA-DHS		4787	68.5	31135	3.62	0.31	0.27	20.0	115	0.22	0.41	0.53	14.6	0.55	19.1	0.06	2.24	0.25

Dissolved (µg/L)	SF3	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
WAR		508	31.6	6226	1.74	1.62	2.33	11.0	53.5	0.31	0.78	7.39	391	1.99	17.4	0.03	2.23	0.39
GCP		503	30.6	5926	2.93	1.53	1.90	12.2	62.1	0.26	0.85	6.66	352	1.80	17.1	0.04	1.18	0.38
WBR		1502	27.7	7472	3.23	2.06	1.30	20.3	50.0	0.56	1.10	6.74	269	2.33	17.7	0.07	1.04	0.28
LSA		1072	24.2	7185	2.93	1.31	1.23	19.5	118	0.43	1.03	7.12	611	2.27	17.5	0.08	1.10	0.52
TRW		2087	33.2	13141	2.54	1.55	1.39	32.5	117	0.57	1.84	10.5	813	2.97	18.3	0.14	1.41	0.64
WGR		2422	33.4	17630	2.54	1.13	1.70	35.6	167	0.48	1.92	7.83	757	2.81	17.7	0.14	1.38	0.62
UWB		1859	27.9	12739	2.00	1.12	0.40	15.6	111	0.71	0.95	9.31	173	2.54	18.3	0.03	1.19	0.61
DWB		1691	30.4	11054	2.39	1.04	0.21	23.8	48.8	0.23	0.55	1.85	33.7	3.60	16.2	0.02	0.73	0.15
HEA-UHS		4813	7.43	30310	1.62	0.21	0.19	16.8	39.9	0.26	0.37	0.26	3.82	0.37	15.6	0.02	0.36	0.09
HEA-DHS		4458	7.80	29360	1.87	0.26	0.11	17.2	32.7	0.19	0.29	0.32	7.48	0.47	15.7	0.02	0.46	0.04

Average percentage difference between duplicates and original samples (total and dissolved trace elements)

Element	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
Average total field duplicate % difference	1%	3%	4%	6%	9%	13%	4%	2%	5%	7%	1%	2%	1%	8%	9%	7%	2%
Average total lab duplicate % difference	0%	0%	1%	4%	2%	8%	5%	2%	8%	11%	2%	1%	3%	6%	11%	7%	1%
Average dissolved field duplicate % difference	1%	12%	0%	7%	2%	9%	1%	17%	2%	17%	22% (7% ignoring one sample)	0%	6%	0%	26% (11% ignoring one sample)	10%	3%
Average dissolved lab duplicate % difference	4%	6%	4%	14%	2%	271% (32% ignoring one sample)	4%	2%	5%	0%	9%	22%	4%	0%	90% (17% ignoring one sample)	22% (4% ignoring one sample)	22% (4% ignoring one sample)

Hardness Modified Trigger Values for stormflow two (Moderate average hardness of 62.8 mg/L as $CaCo_3$):

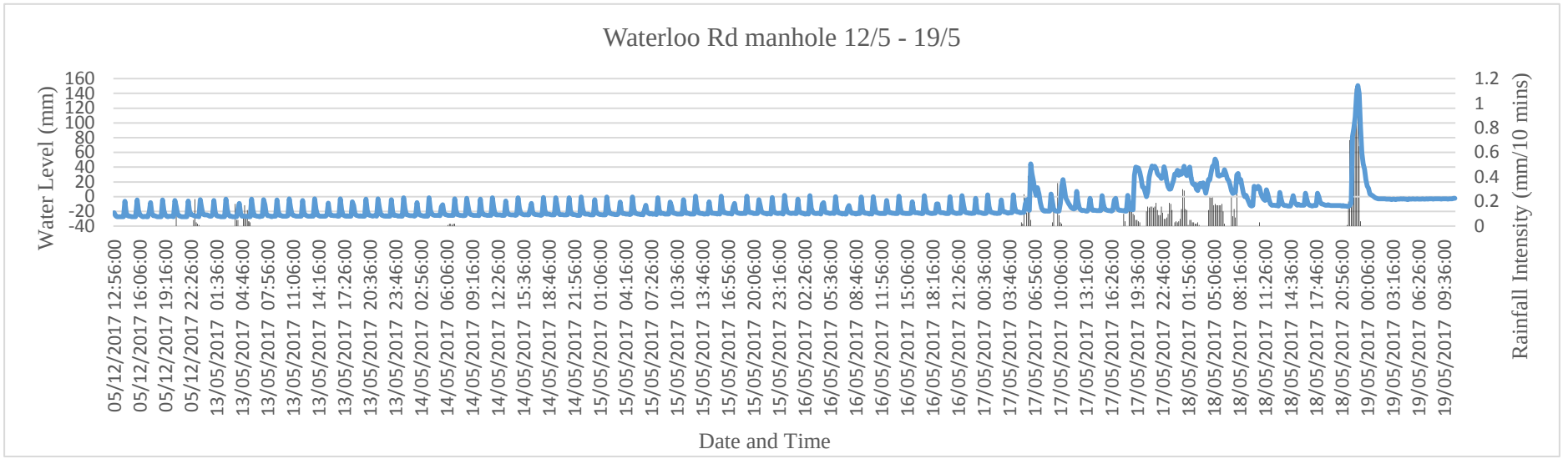
Hardness Dependent algorithms used:

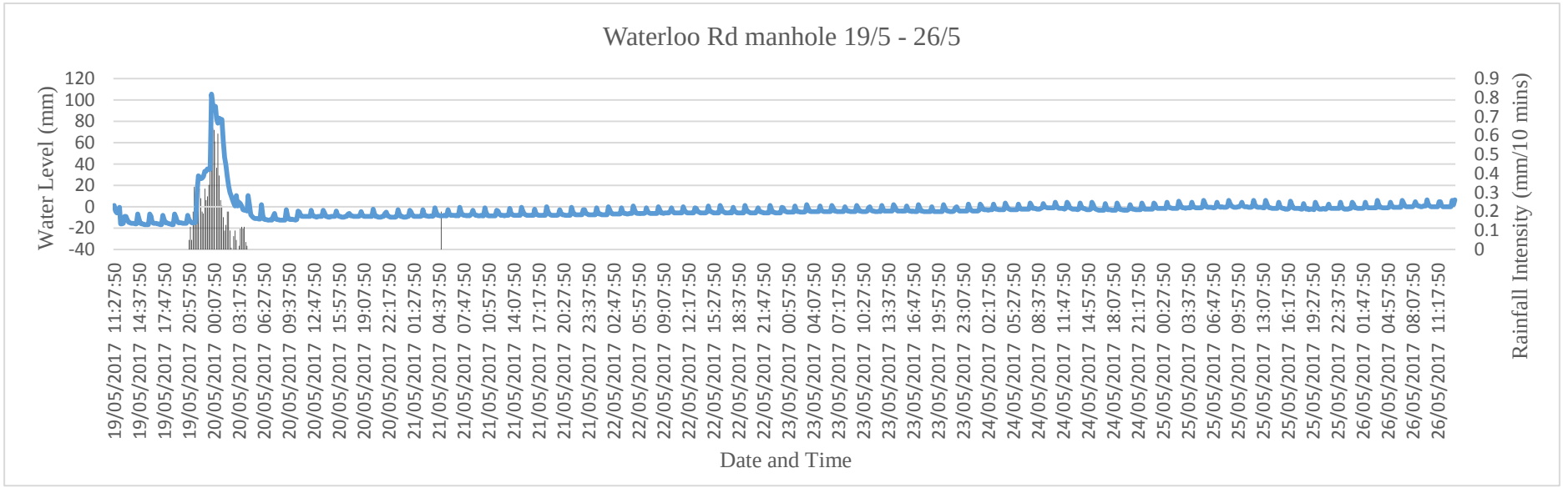
Metal	Algorithm
Cadmium	Trigger Value (Hardness/30)$^{0.89}$
Chromium (III)	Trigger Value (Hardness/30)$^{0.82}$
Copper	Trigger Value (Hardness/30)$^{0.85}$
Lead	Trigger Value (Hardness/30)$^{1.27}$
Nickel	Trigger Value (Hardness/30)$^{0.85}$
Zinc	Trigger Value (Hardness/30)$^{0.85}$

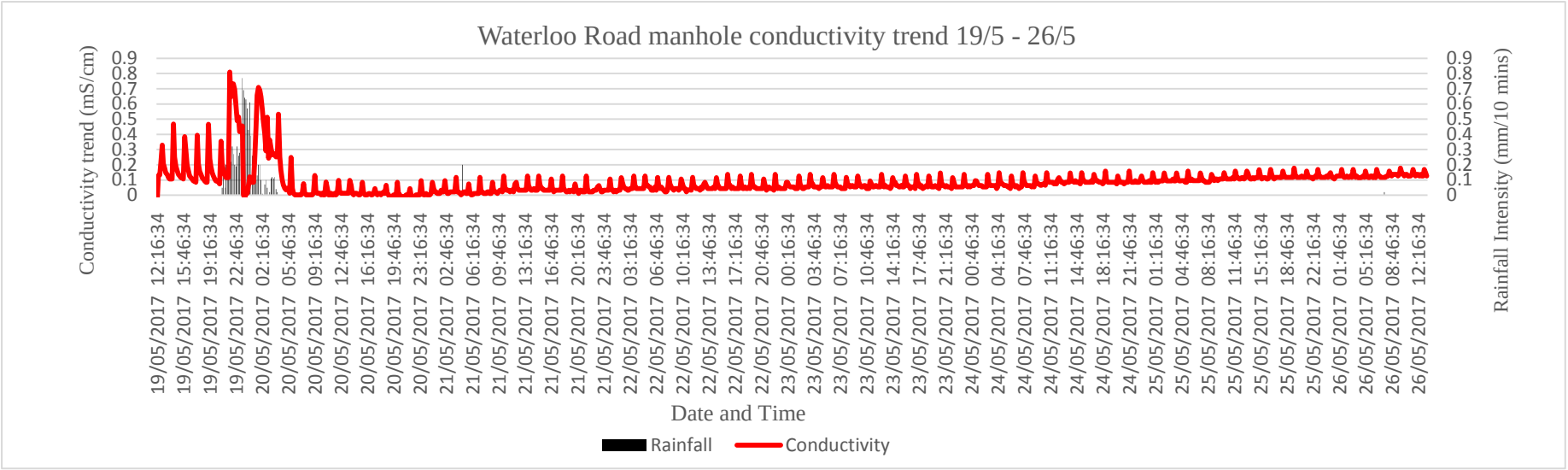
Modified guideline values for stormflow two:

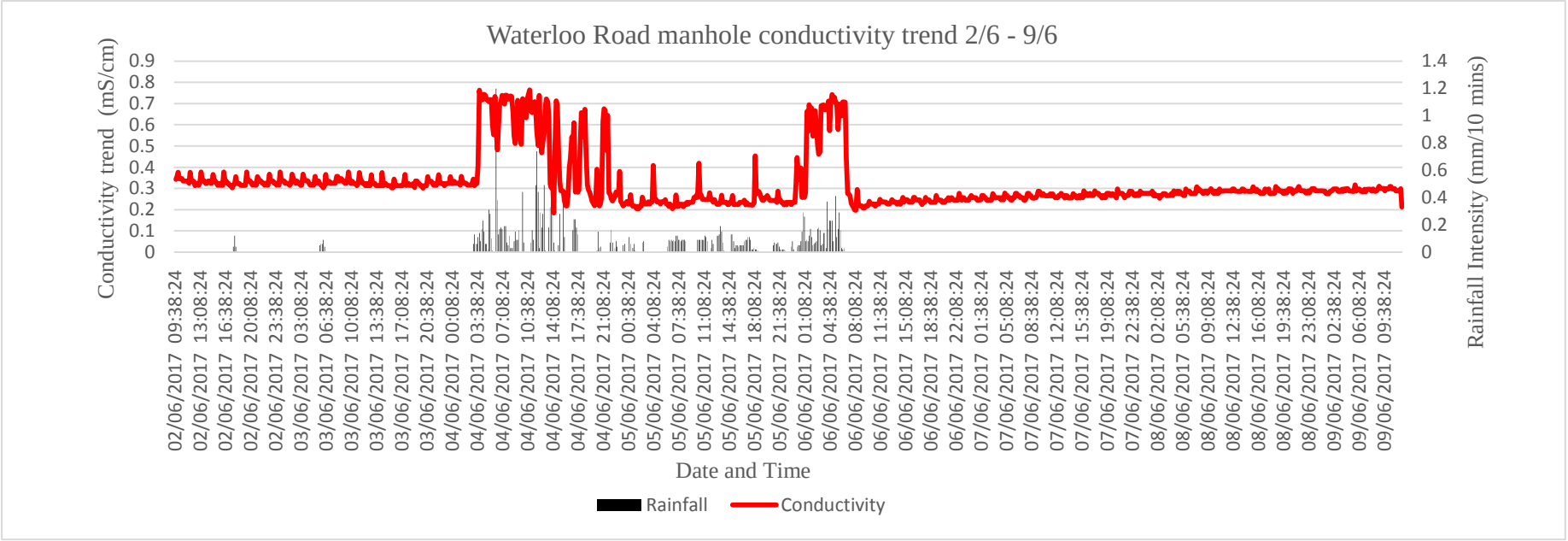
Metal	Normal 80% guideline	Hardness-modified 80% guideline
Cadmium	0.8 µg/L	24 µg/L
Chromium	40 µg/L	73.3 µg/L
Copper	2.5 µg/L	4.68 µg/L
Lead	9.4 µg/L	24 µg/L
Nickel	17 µg/L	31.9 µg/L
Zinc	31 µg/L	58.09 µg/L

Appendix 5- Weekly logging data throughout the Haytons Stream catchment

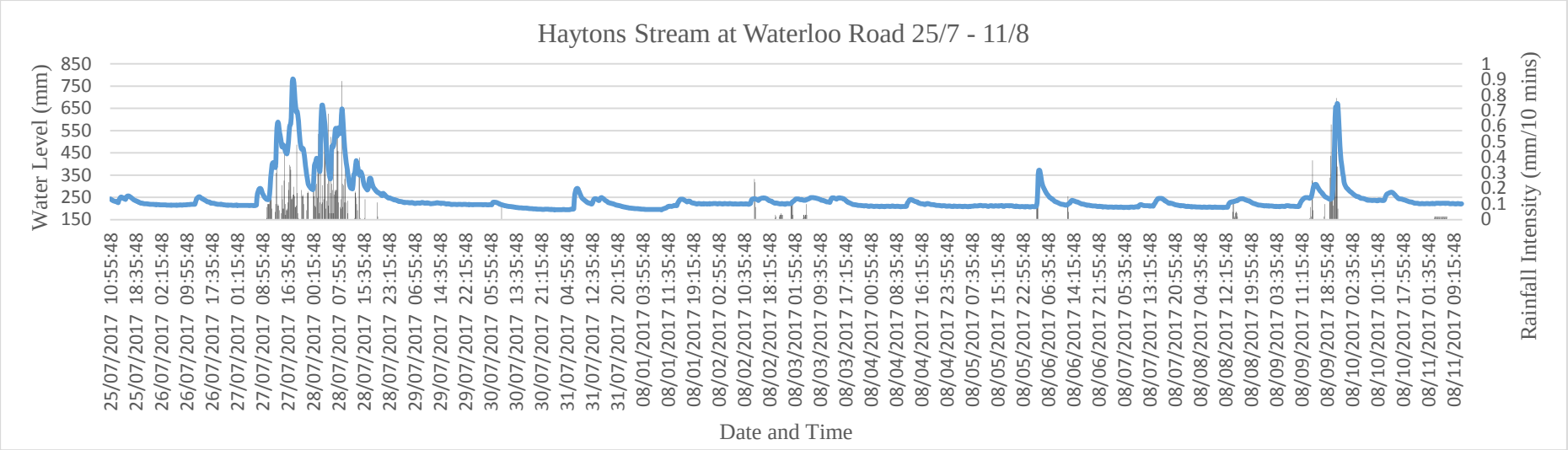


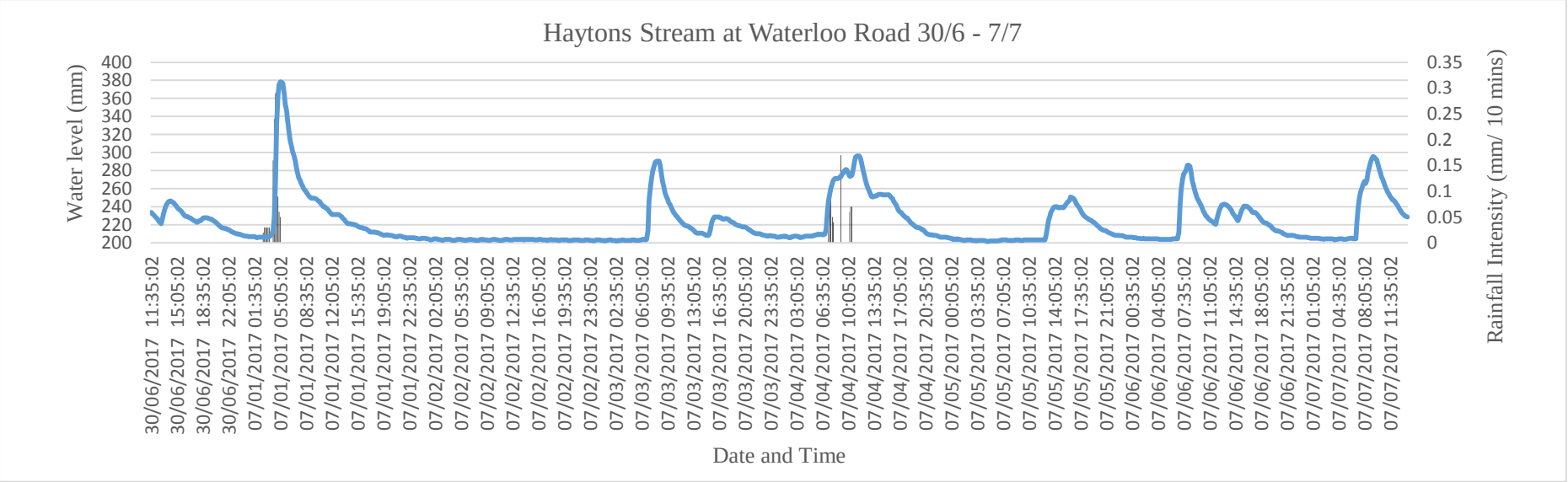


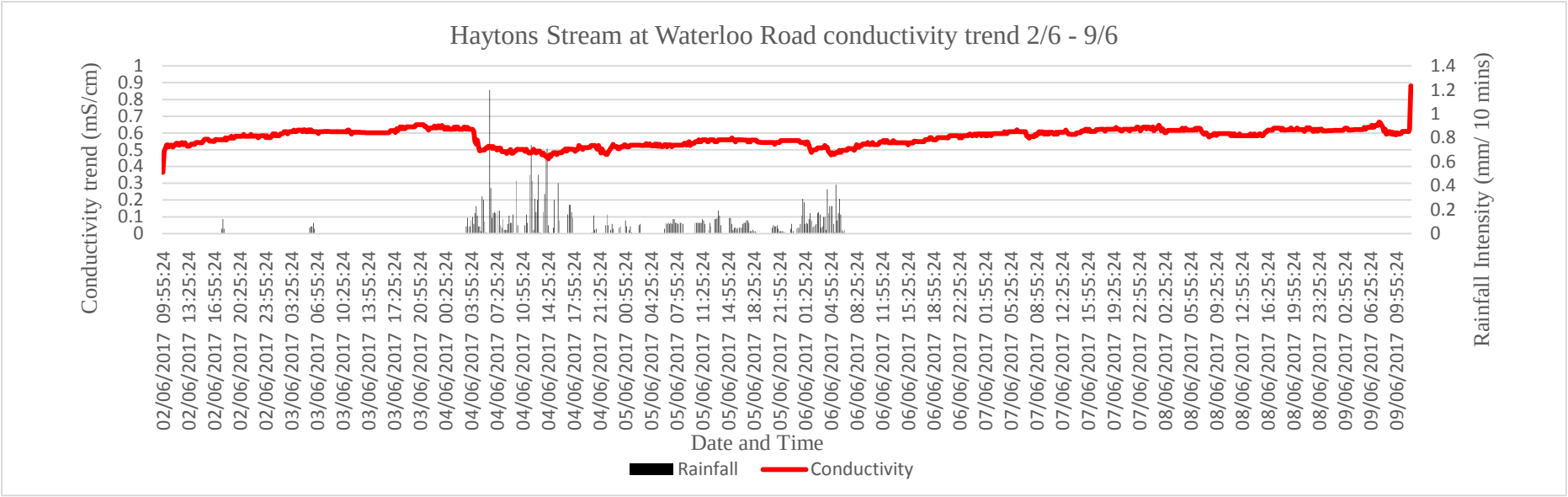

Waterloo Road manhole conductivity trend 19/5 - 26/5
Conductivity trend (mS/cm)
Rainfall Intensity (mm/10 mins)
Date and Time
Rainfall
Conductivity

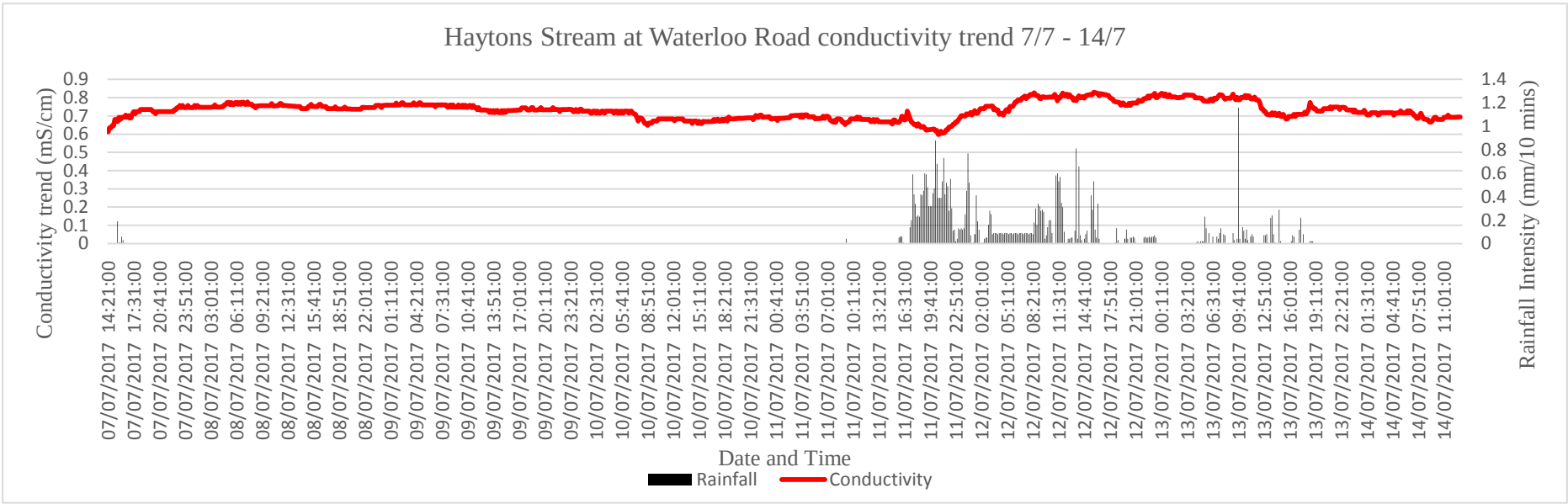

Waterloo Road manhole conductivity trend 2/6 - 9/6
Conductivity trend (mS/cm)
Rainfall Intensity (mm/10 mins)
Date and Time
Rainfall
Conductivity

Haytons Stream at Waterloo Road:

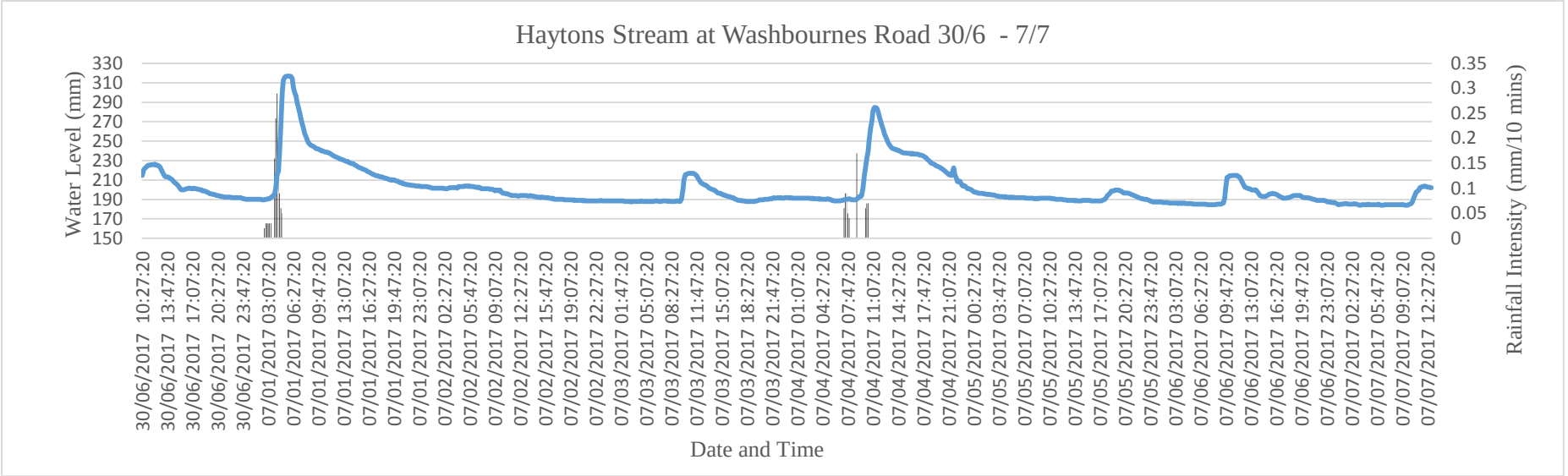


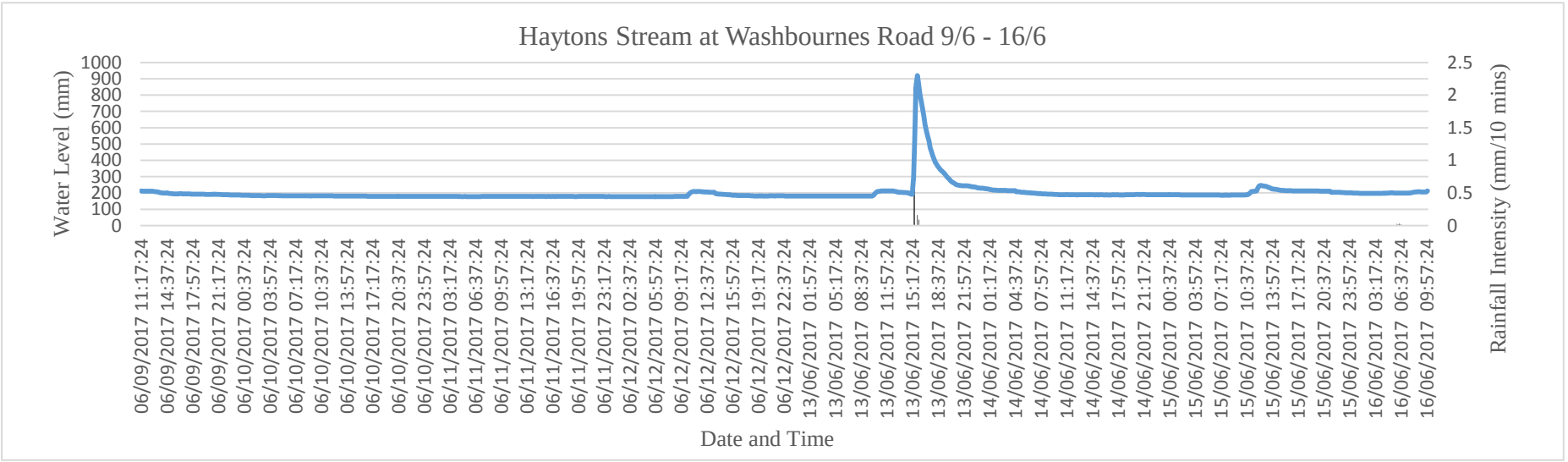


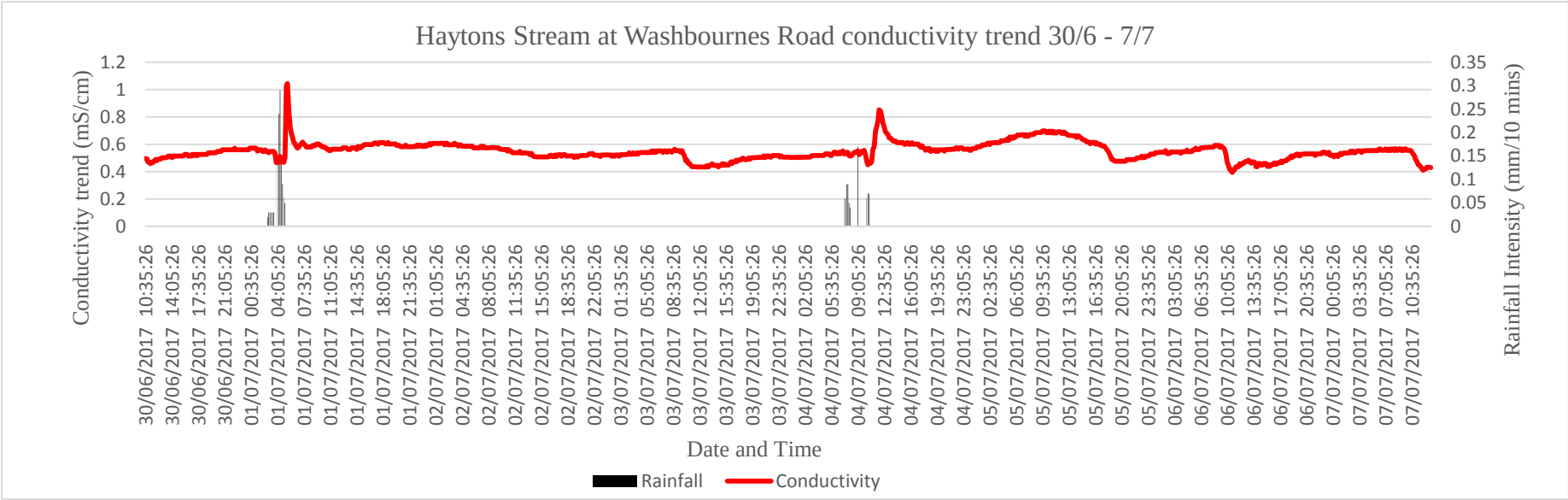

Haytons Stream at Waterloo Road conductivity trend 2/6 - 9/6
Conductivity trend (mS/cm)
Rainfall Intensity (mm/ 10 mins)
Date and Time
Rainfall
Conductivity

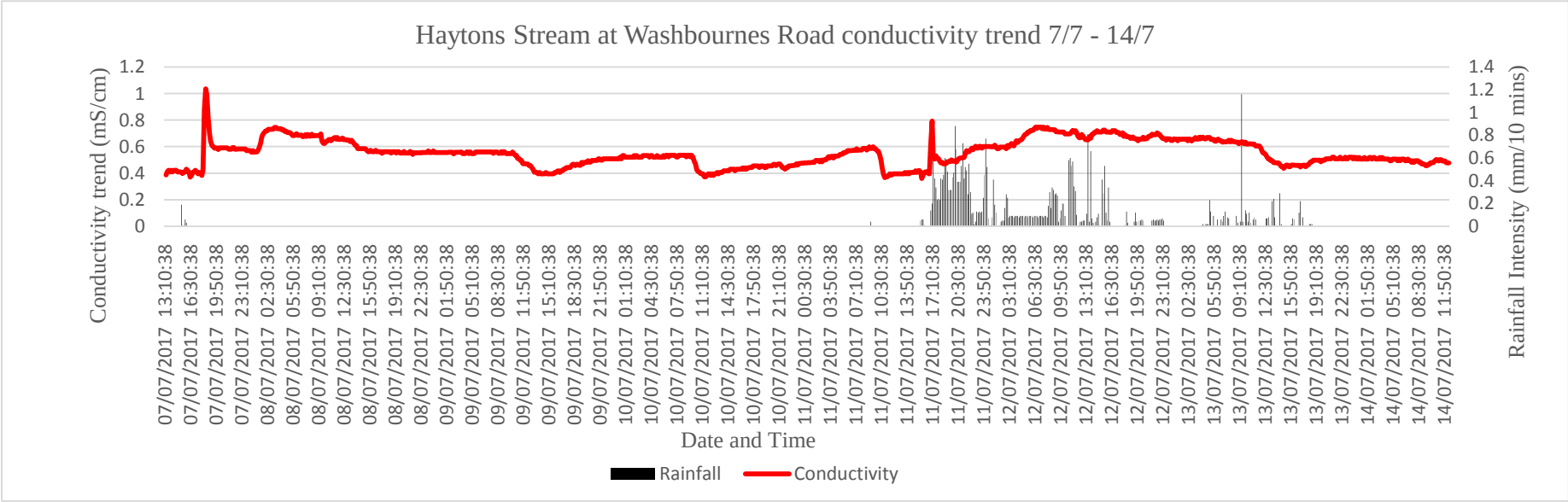

Haytons Stream at Waterloo Road conductivity trend 7/7 - 14/7
Conductivity trend (mS/cm)
Rainfall Intensity (mm/10 mins)
Date and Time
Rainfall
Conductivity

Haytons Stream downstream of Washbournes Road

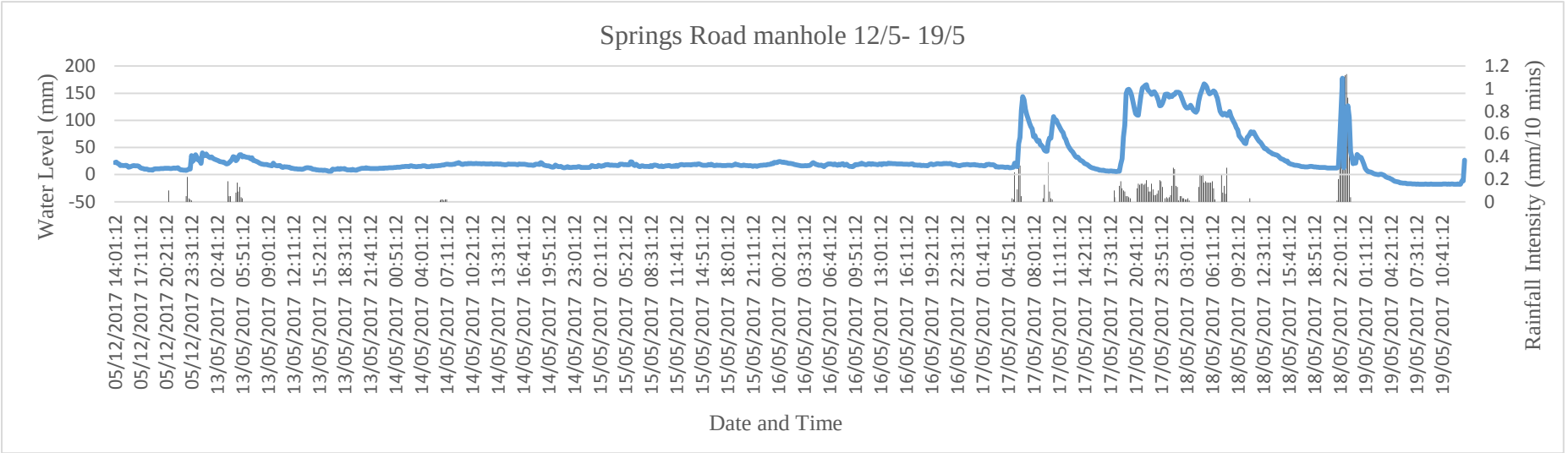


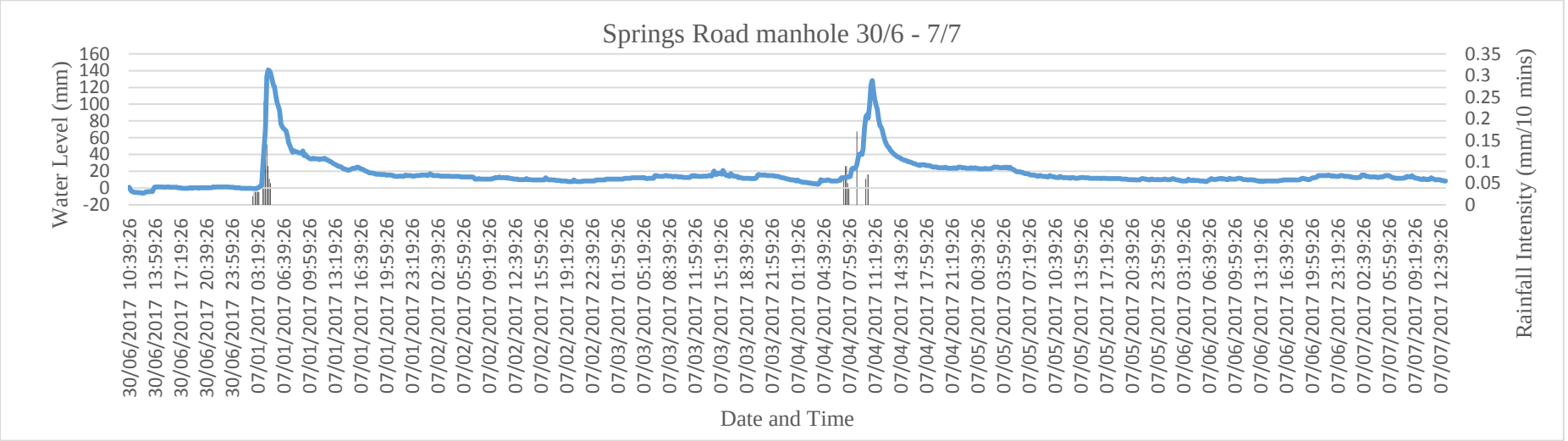



Haytons Stream at Washbournes Road conductivity trend 30/6 - 7/7
Conductivity trend (mS/cm)
Rainfall Intensity (mm/10 mins)
Date and Time
Rainfall
Conductivity

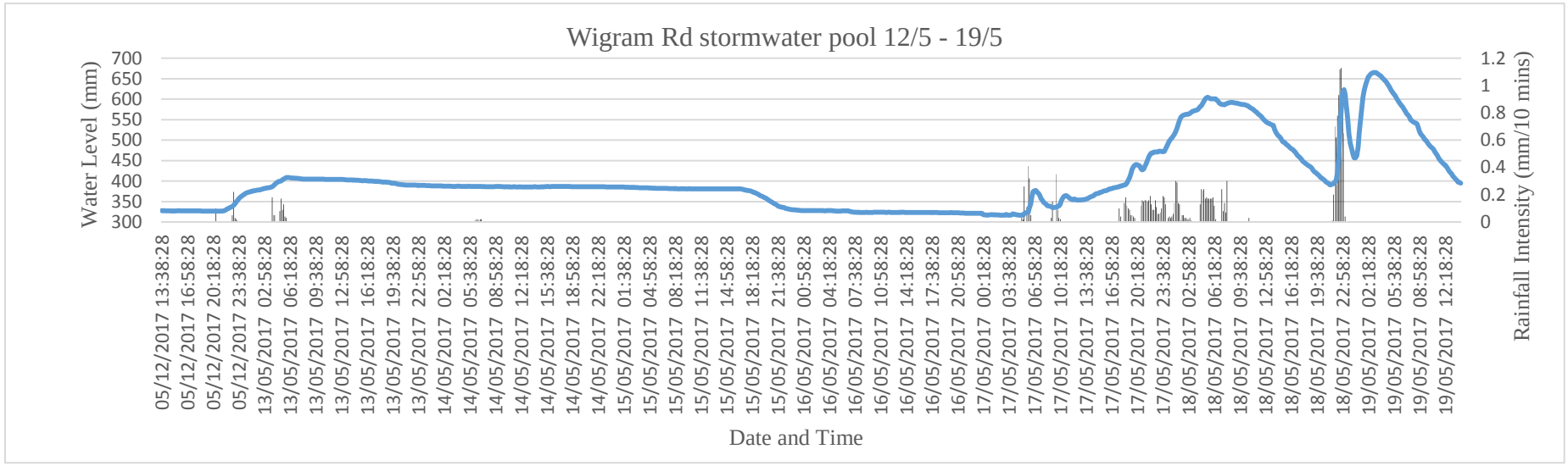

Haytons Stream at Washbournes Road conductivity trend 7/7 - 14/7
Conductivity trend (mS/cm)
Rainfall Intensity (mm/10 mins)
Date and Time
Rainfall
Conductivity

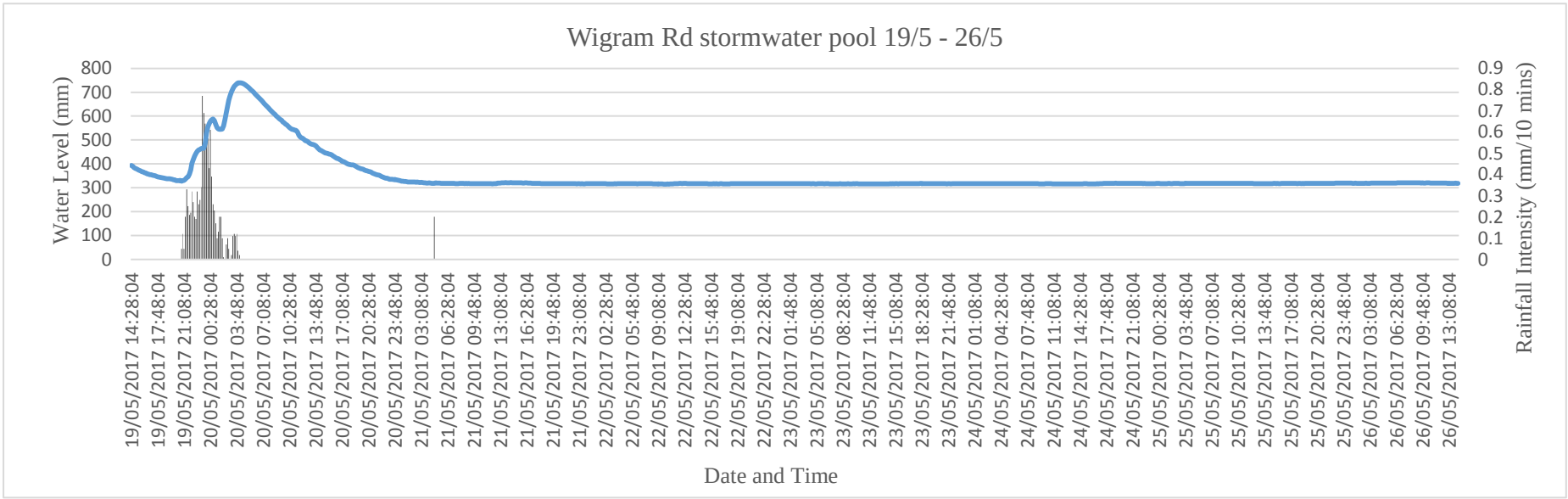
Springs Road manhole

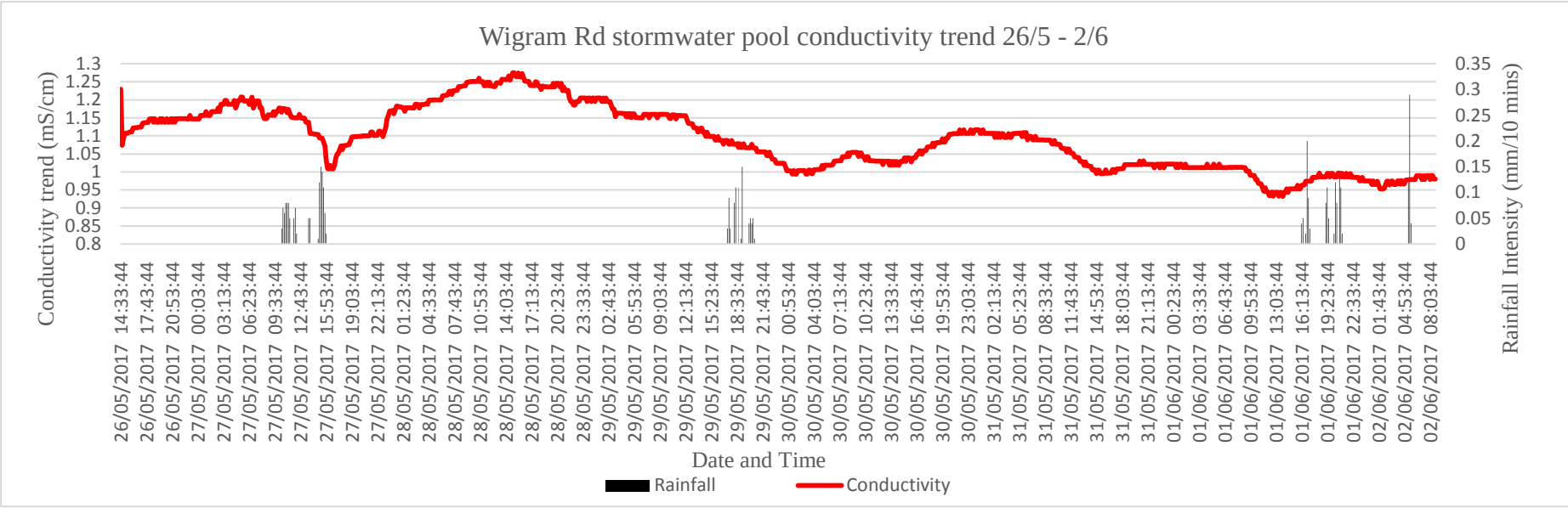


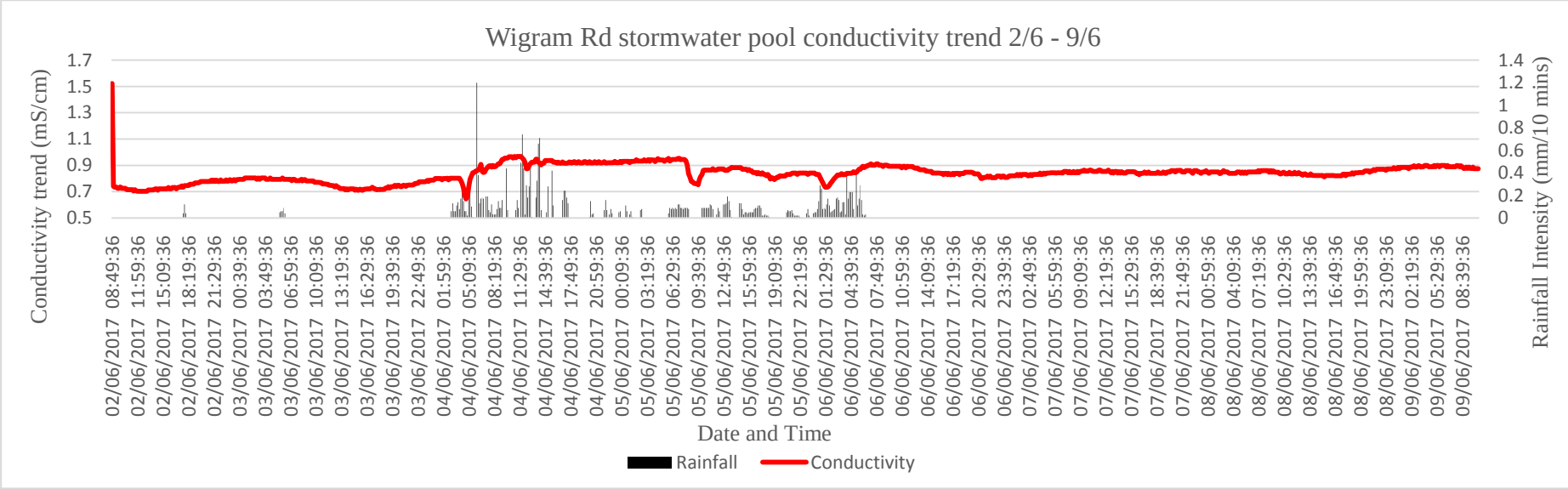


Wigram Road

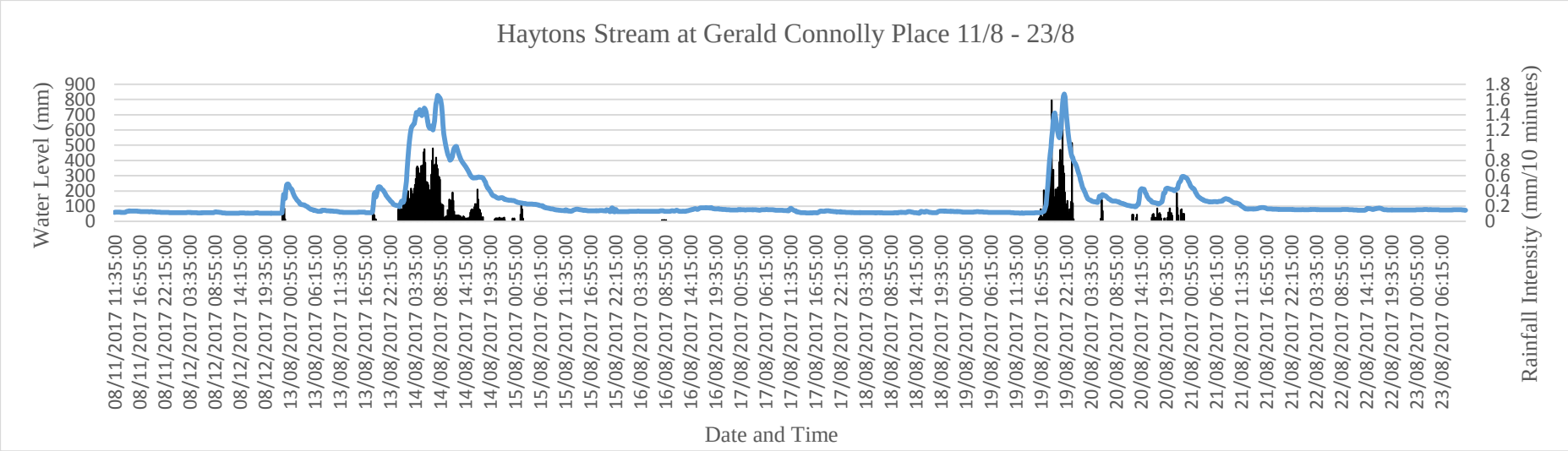

Wigram Rd stormwater pool 12/5 - 19/5
Water Level (mm)
Rainfall Intensity (mm/10 mins)
Date and Time

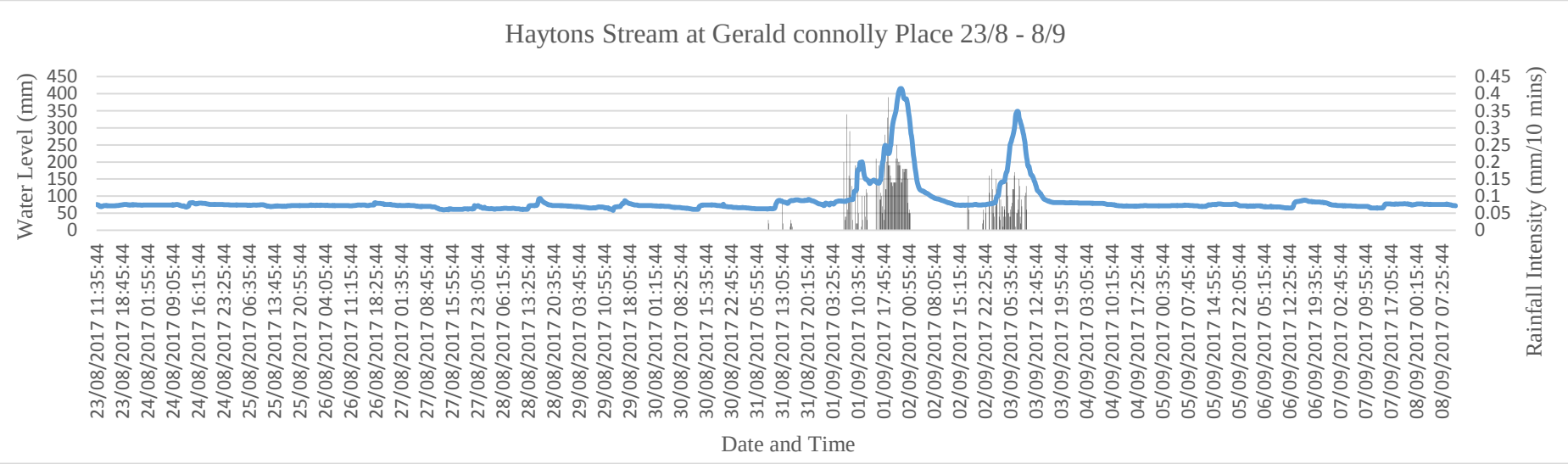

Wigram Rd stormwater pool 19/5 - 26/5
Water Level (mm)
Rainfall Intensity (mm/10 mins)
Date and Time

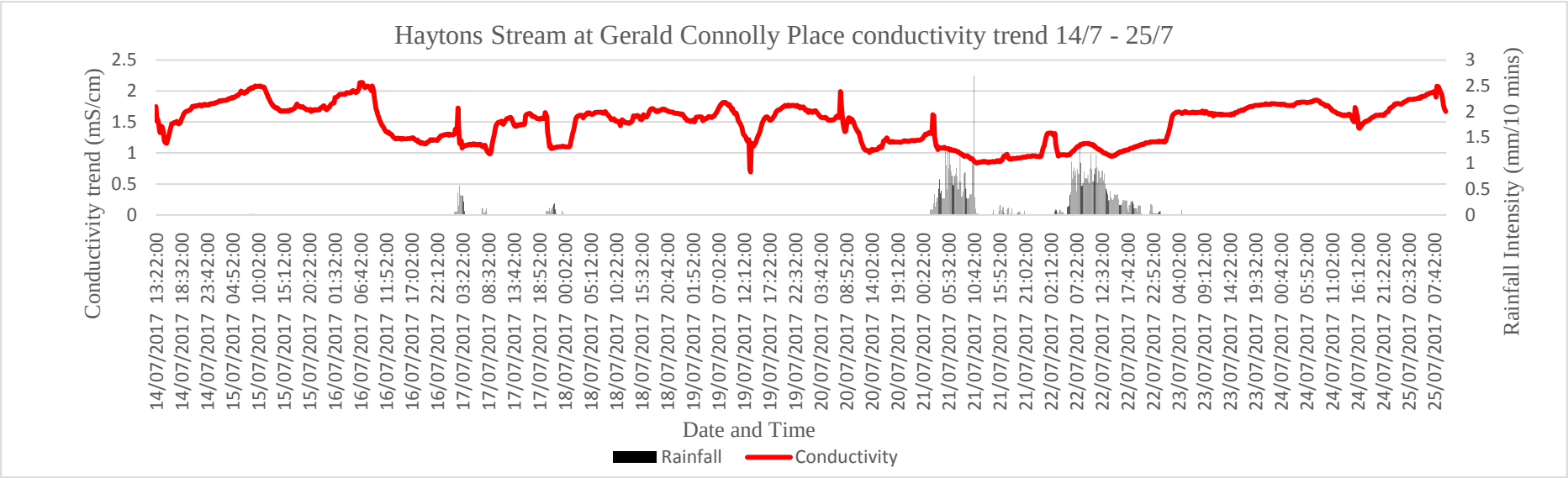

Wigram Rd stormwater pool conductivity trend 26/5 - 2/6
Conductivity trend (mS/cm)
Rainfall Intensity (mm/10 mins)
Date and Time
Rainfall
Conductivity

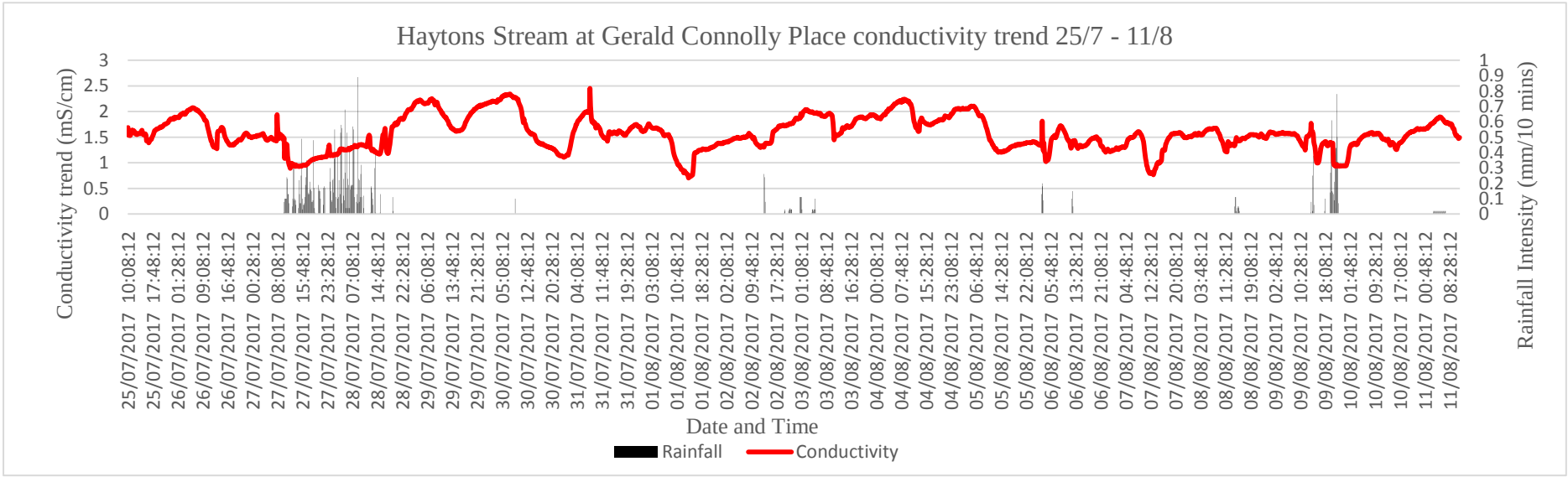

Wigram Rd stormwater pool conductivity trend 2/6 - 9/6
Conductivity trend (mS/cm)
Rainfall Intensity (mm/10 mins)
Date and Time
Rainfall
Conductivity

Haytons Stream at Gerald Connolly Place






Haytons Stream at Gerald Connolly Place conductivity trend 14/7 - 25/7
Conductivity trend (mS/cm)
Rainfall Intensity (mm/10 mins)
Date and Time
Rainfall
Conductivity


Haytons Stream at Gerald Connolly Place conductivity trend 25/7 - 11/8
Conductivity trend (mS/cm)
Rainfall Intensity (mm/10 mins)
Date and Time
Rainfall
Conductivity

Appendix 6- Full contaminant concentrations found within industrial stormwater sumps

Sump	TSS	NH4-N	TKN	NNN	TN	DRP	TP	COD
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg O_2/L
1	77.0	2.90	6.30	0.21	6.51	0.97	1.79	52.0
2	2860	0.52	17.0	0.02	17.0	0.06	2.50	3200
3	165	0.58	2.00	0.67	2.67	0.12	0.43	22.0
4	521	0.16	2.20	0.11	2.31	0.04	0.55	260
5	-	1.86	12.4	0.50	12.9	0.99	5.20	470
6	573	1.61	8.50	0.12	8.62	0.01	1.48	370
7	94.6	0.01	1.48	0.54	2.02	0.05	0.57	38.0
8	4.00	1.56	3.40	1.56	4.96	0.02	0.10	11.0
9	69.5	1.11	6.00	0.98	6.98	0.18	0.68	114

Sump (total metals in µg/L)	Mg	Al	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
1	1872	2974	18159	41.0	11.5	5.45	139	8573	2.19	12.2	18.1	392	3.40	20.7	0.52	3.03	6.18
2	14254	37657	231534	1639	60.0	237	6045	262009	245	374	989	35286	32.3	61.8	37.0	31.9	620
3	3130	10439	23578	765	25.7	12.4	217	10139	3.55	6.82	20.1	221	6.26	3.95	0.19	2.92	12.8
4	1561	2316	17270	91.6	12.0	7.57	89.2	3438	1.29	5.38	119	353	5.77	15.4	0.40	17.3	45.0
5	15390	60440	45480	3979	103	123	1656	82723	30.7	62.1	245	1602	39.8	15.1	0.87	115	214
6	3854	12207	39223	320	24.0	39.5	739	38365	12.3	32.6	322	2461	12.2	20.9	4.95	7.42	280
7	941	2023	14906	106	11.5	21.2	79.0	4963	5.94	12.4	68.3	2206	8.30	2.47	0.23	2.15	54.0
8	941	121	21167	0.00	29.8	1.78	28.0	240	0.95	2.57	7.67	286	1.59	26.5	0.13	1.87	19.0
9	2466	1344	25066	64.0	11.9	6.04	211	14367	2.46	12.9	119	599	3.78	3.39	0.53	10.4	9.38

Volatile Organic Compounds (VOCs) above detection limits in sumps (brackets show concertation in mg/L)

Sump 1	Sump 2	Sump 3	Sump 4	Sump 5	Sump 6	Sump 7	Sump 8	Sump 9
Toluene (0.0007)	Toluene (0.004)	Toluene (0.0009)	Toluene (0.0008)	Toluene (0.0007)	Benzene (0.0009)	Benzene (0.0004)		Toluene (0.0029)
	m&p- xylene (0.012)	Chlorobenzene (0.0031)		m&p-xylene (0.0009)	Ethylbenzene (0.0010)	Toluene (0.0013)		M&p- Xylene (0.0005)
	o-xylene (0.03)	1,4-Dichlorobenzene (0.0018)		o-Xylene (0.0008)	Toluene (0.0119)	m&p-Xylene (0.0006)		o- Xylene (0.0003)
	Dichloromethane (0.013)	Chloroform (0.0007)		Dichloromethane (0.0009)	m&p-Xylene (0.003)	o-Xylene (0.0004)		1,2,4-Trimethylbenzene (0.0003)
	Tetrachloroethene (0.003)			1,2,4-Trimethylbenzene (0.0008)	o-Xylene (0.0028)	1,2,4-Trimethylbenzene (0.0004)		
	1,2,4-Trimethylbenzene (0.03)			1,3,5-Trimethylbenzene (0.0003)	Dichloromethane (0.036)			
				Acetone (0.06)	Isopropyl benzene (0.0005)			
				4-Methylpentan-2-one (0.034)	n-Propyl benzene (0.0013)			
				Carbon disulphide (0.0002)	1,2,4-Trimethylbenzene (0.0192)			
					1,3,5-Trimethylbenzene (0.007)			
					Acetone (0.14)			
					Carbon disulphide (0.00168)			
					Naphthalene (0.0006)			